Interim Report No. 1 | *June 1964 to August 1965*

DEVELOPMENT OF SPECIFICATIONS FOR POLYMERIC MATERIALS

Prepared for:

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

JPL CONTRACT NO. 950745
UNDER NAS7-100

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

*SRI

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This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

August 9, 1965

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JPL Cognizant Engineer: HUGH G. MAXWELL

SRI Project Supervisor: R. F. MURACA

SRI Project No. ASD-5046

Approved: R. F. MURACA, DIRECTOR
ANALYSES AND INSTRUMENTATION

H. G. MAXWELL, JPL
COGNIZANT ENGINEER

Copy No. .....

FOREWORD

This Interim Report summarizes the work performed by Stanford Research Institute during the period June 1964 to August 1965 under Contract No. 950745 for the Jet Propulsion Laboratory of the California Institute of Technology.

Mr. Hugh G. Maxwell of the Jet Propulsion Laboratory's Materials and Methods Group was Cognizant Engineer for the Project.

The technical effort at Stanford Research Institute was under the supervision of Dr. R. F. Muraca, Director, Analyses and Instrumentation.

Work on the development of specification procedures, including technical and editorial assistance in the establishment of test and materials specifications, was performed within the Department of Analyses and Instrumentation under the direction of Dr. R. F. Muraca; participants in this work were: F. Church, E. Lawler, and J. Whittick.

The preparation of preliminary specifications recommendations and exploratory work on the weight-loss behavior of selected polymeric materials were performed within the Polymer Sciences Group under the direction of Dr. D. J. Lyman; participants in this work were: J. Black, M. Golub, J. Heller, and D. Parkinson.

ABSTRACT

Stanford Research Institute, Menlo Park, California
DEVELOPMENT OF SPECIFICATIONS FOR POLYMERIC MATERIALS
Interim Report No. 1, June 1964 to August 1965
R. F. Muraca, et al., August 9, 1965,
(NASA Contract No. NAS7-100; JPL Contract 950745; SRI Project ASD-5046)

A summary is given of work leading to recommendations for preparation of specifications for selected polymeric materials to be used in spacecrafts.

A design drawing and photographs are presented for a standardized vacuum-weight-loss apparatus and suggestions are made toward a standardized thermal-vacuum weight-loss procedure. Procedures and data are summarized for chemical and physical testing of a series of epoxy adhesives.

A discussion is given of exploratory work on the weight-loss behavior of epoxy, silicone, and fluorocarbon polymers in vacuo at temperatures of 150 °C and 200 °C.

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I. INTRODUCTION

This Interim Report summarizes the work performed under JPL Contract 950745, SRI Project ASD-5046, during the period June 1964 to August 1965.

The broad objective of this program is to provide assistance to the Jet Propulsion Laboratory's Materials and Methods Group in the development of materials specifications and test procedures for polymeric materials which are considered for use in spacecrafts. The selection of materials to be investigated and the extent of effort are determined by the JPL Cognizant Engineer.

Sections II and III summarize the work performed on the design and construction of a standardized vacuum weight loss apparatus for test specifications, and an investigation of the procedures for physical and chemical qualification tests on epoxy adhesives in order to make recommendations for materials specifications.

Section IV of this report summarizes the work performed on the accumulation of data relative to the properties of epoxy, silicone, and fluorocarbon polymers and their weight-loss behavior in a vacuum environment at elevated temperatures. Most of the work performed on these polymers has been reported in prior publications, in great detail; however, only the best data and conclusions are recorded in this report.

Future work is discussed in Section V.

II. DEVELOPMENT OF STANDARDIZED PROCEDURES FOR VACUUM WEIGHT LOSS DETERMINATION OF POLYMERIC MATERIALS

The loss of weight of polymeric materials when exposed to a vacuum-thermal environment is an important criterion in the acceptance of these materials for use in spacecrafts since the release of volatile substances may affect desirable mechanical, physical, or electrical properties. As shown in Table I, a great variety of polymeric materials are potential candidates for spacecraft use, based on recommended long-time service temperature limits. Selection of the most suitable polymeric materials is then dependent on behavior at specified temperature in a vacuum environment.

Vacuum weight loss data have been reported for many polymeric materials which have been considered for use in spacecrafts or high vacuum systems (References 1-20). However, the conditions of pressure in these reported results have ranged from 10^{-3} torr to 10^{-9} torr, temperatures have ranged from 25 ^{o} to 200 ^{o}C, and exposure times have ranged from 24 hours to 1000 hours. Additionally, a wide range of apparatuses and procedures have been employed, for example, weighing before and after exposure in a simple bell jar, or monitoring weight constantly via a vacuum thermogravimetric balance. Thus, it is difficult if not impossible to utilize the reported data as specifications requirements.

Requirements for compliance with weight loss criteria can only be based on the establishment of a standardized apparatus and procedure which are easily duplicated by testing laboratories. Therefore, the three-fold purpose of this phase of the program is:

(1) To design and construct a vacuum weight loss apparatus which will ensure maximum pumping efficiency and thermal control with a minimum of construction expense and complexity;

(2) To determine the conditions of temperature, pressure, and exposure time which will provide the most valid and meaningful weight loss data;

TABLE I

SERVICE TEMPERATURE LIMITS AT ATMOSPHERIC PRESSURE FOR REPRESENTATIVE CLASSES OF POLYMERIC MATERIALS

(Manufacturer's Recommendations)

Polymer Class	Long-Time Service Temperature Limit, (to) °C					
	125	150	175	200	250	275
Chlorosulfonated Polyethylene Elastomers	X					
Ethylene-Propylene Elastomers	X					
Fluoroelastomers				X		
Isobutylene-Isoprene Elastomers		X				
Polyurethane Elastomers (Millable)	X					
Silicone Elastomers (Millable					X	
Silicone Elastomers, Liquid and Paste					X	
Fluorocarbon Plastics	X			X		X
Film Polyester		X				
Fiber Polyester		X				
Polycarbonate	X					
Epoxy	X	X	X	X		
Polyimide Resins						X
Polyamide Resins			X			
Chlorinated Polyether Plastic	X					

(3) To establish a procedure for performing weight loss determinations.

Based on the results of this work, recommendations will be made for incorporation into JPL Specification No. ZTF-4000-0002, "Test Specifications: Vacuum Weight Loss of Polymeric Materials."

Apparatus

The vacuum weight loss apparatus is shown in the photograph in Figure 1. A design drawing, including the parts list, is given in Figure 2 so that the apparatus may be readily duplicated.

As shown in Figures 1 and 2, the apparatus accommodates duplicate samples under identical vacuum-thermal conditions; the large-bore stopcocks ensure maximum rate of evacuation on each sample and valid pressure measurements (made via a gage directly above the sample chamber).

The purpose of the well near the joint of each sample chamber is to collect substances which may condense at cooler temperatures and to prevent re-deposit of these substances on the samples. One-mm stopcocks are affixed to the arms leading from the sample chambers to permit venting at termination of the tests.

Glass hooks have been attached to the caps of each chamber so that samples may be suspended directly by wires or in glass containers. (In view of the anticipated reactivity of some polymeric materials with wire material, Nichrome wires have been gold-plated in order to provide an inert contact surface; platinum wire, of sufficient strength, could also be used.

A good grade of high-temperature vacuum grease is used in order to obviate difficulties created by channeling or outgassing (silicones); "Apiezon- T" or equivalent has been found satisfactory.

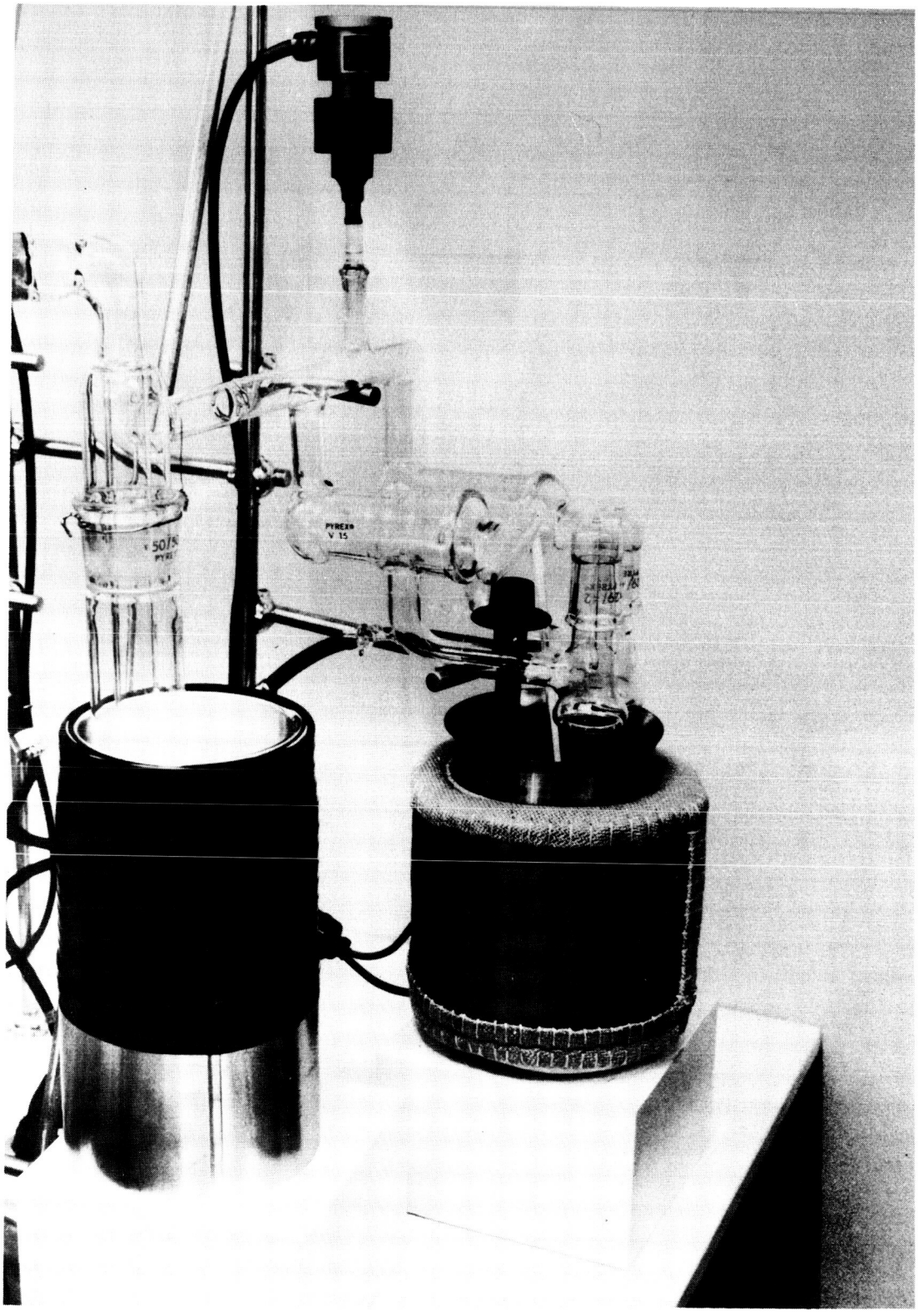

FIG. 1 PHOTOGRAPH OF VACUUM WEIGHT LOSS APPARATUS

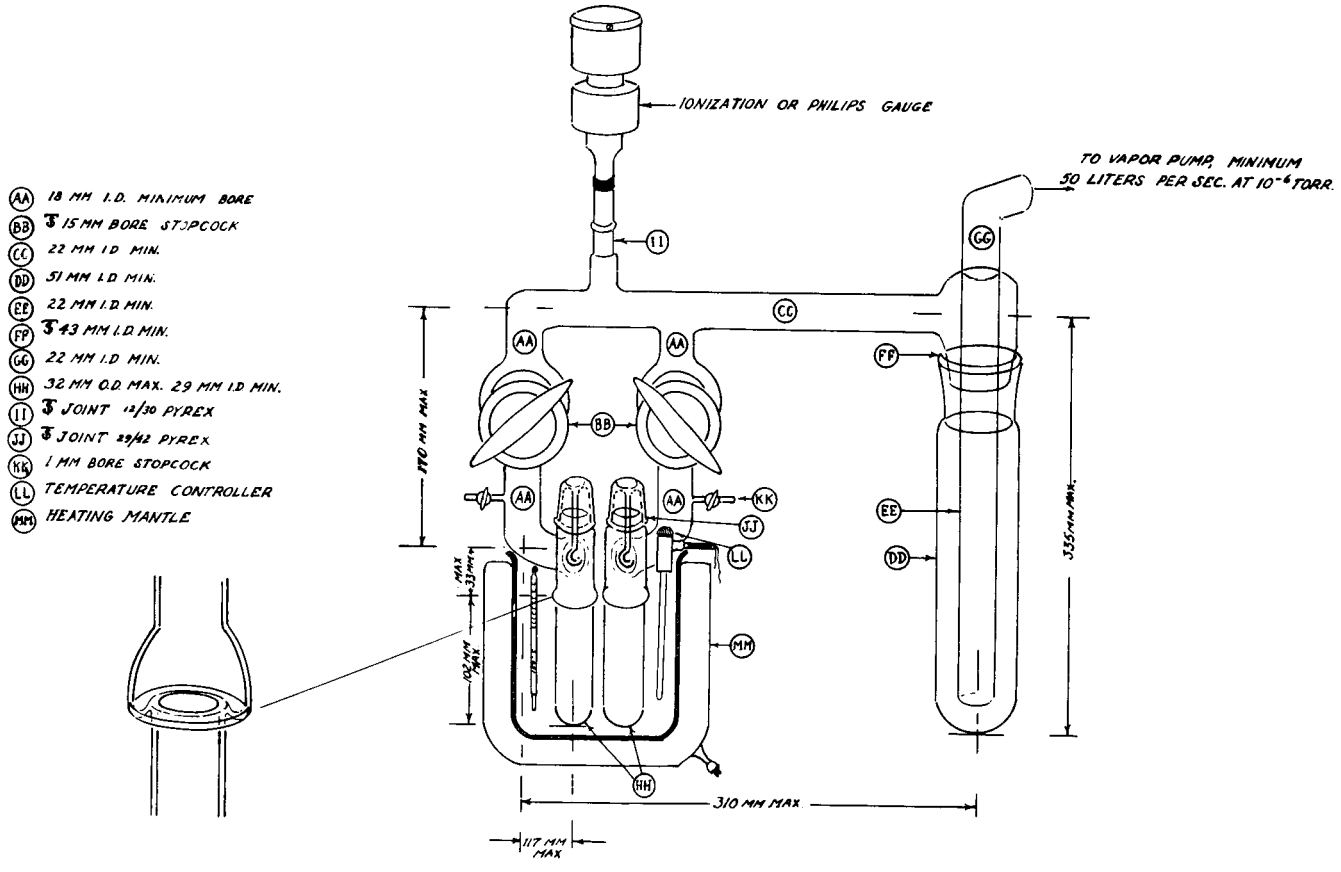

FIG. 2 VACUUM WEIGHT LOSS APPARATUS

The sample chambers are immersed in Fisher bath wax contained in stainless beakers fitted with heating mantles; temperature is maintained by a thermoregulator-variable transformer system. The input to the heating mantles is adjusted so that the wax temperature is maintained at 125 ^{o}C with only minimal control afforded by the thermoregulator.

Vacuum and Control System

Each vacuum weight loss apparatus is attached to a primary manifold leading directly to the pumping system. Figure 3 illustrates a vacuum system consisting of four pumping stations of the kind shown in Figure 1. This arrangement has been set up in order to facilitate the generation of copious data for determining parameters which eventually will be used to establish materials specifications limits. The primary manifold has sufficient pumping speed to accommodate the four units. The primary manifold is a 6-inch glass pipe leading to the fore pump via a water-cooled baffle and a 6-inch diffusion pump. Specifications for this vacuum and control system which will accommodate four vacuum weight loss apparatuses are as follows:

Fore pump: 0.5 liters/second at 10^{-3} torr
Diffusion pump: 1400 liters/second at 10^{-5} torr
Water-cooled baffle: Chevron-ring type
Vacuum gages: 0.25 to 1 x 10^{-7} torr
Temperature controller: 95 to 200 $\pm$ 2 ^{o}C
Heating mantles: 95 to 200 ^{o}C

Operating Conditions

The wax baths have been adjusted to maintain a temperature of 125 ^{o}C since prior work has shown that most polymeric materials do not undergo decomposition at this temperature.

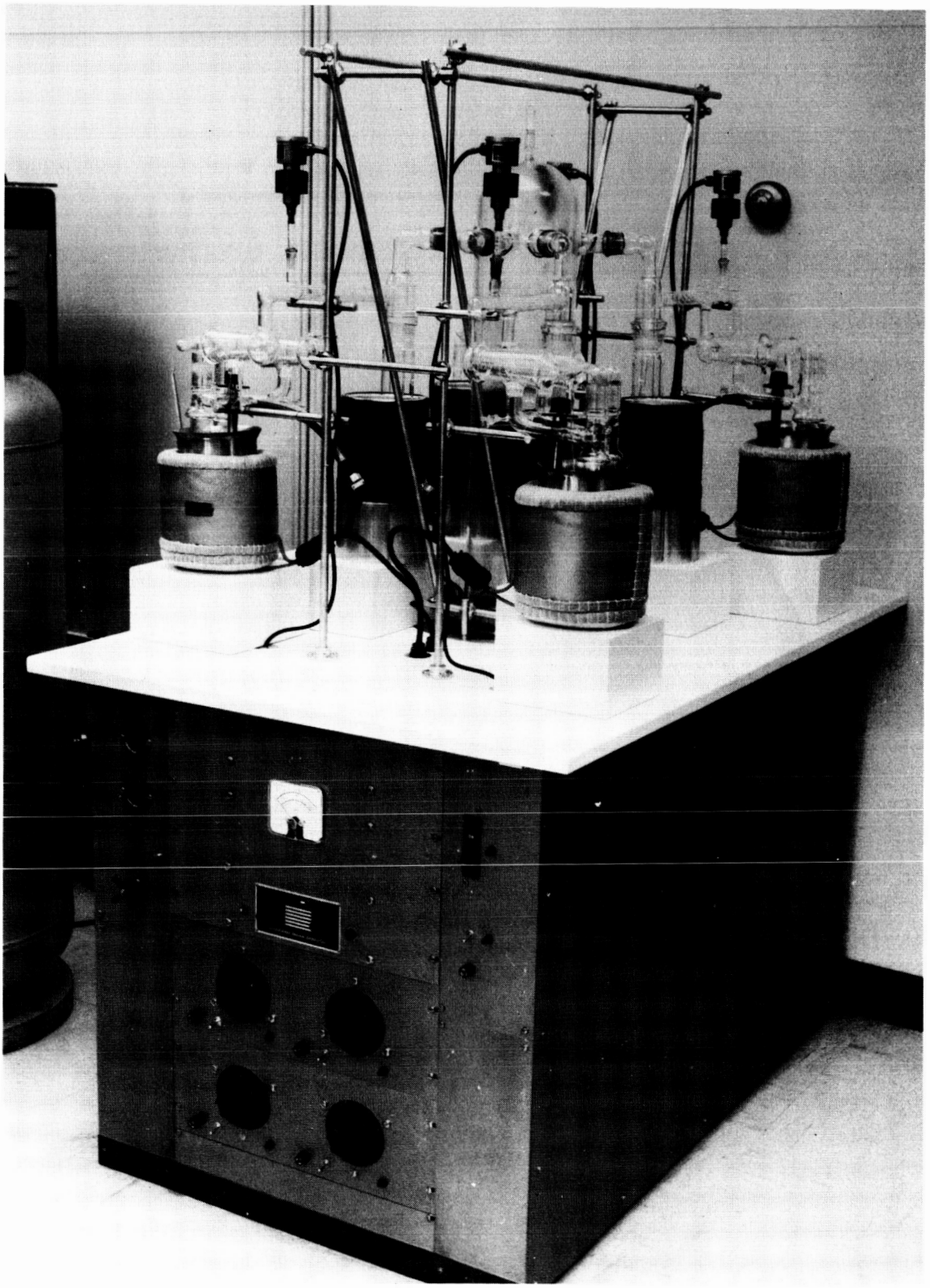

FIG. 3 VACUUM SYSTEM WITH VACUUM WEIGHT LOSS APPARATUSES

Specification recommendations will involve the determination of the slope of the weight loss curve for a specified interval of time, as well as actual weight loss values. The assemblies have been designed so that one sample may be removed after, say, 72 hours and the duplicate after 96 hours. This first approach is made in consideration of the time involved for testing laboratories and elimination of need for "week-end" servicing of traps, etc. The choice of at least a 72-hour interval is based on prior work (Ref. 11) which has shown that the maximum weight loss for most substances occurs within a 48-hour interval and that measurements made in the 1- to 48-hour interval are not as reproducible nor reliable as those after longer exposure times when the slope of the weight loss curve becomes relatively constant.

Procedure

Preliminary recommendations for test procedure have been made. Actual test specification operation is being initiated at the present time; as work progresses, necessary modifications of procedure, if any, will be submitted for consideration as revisions to the accepted test specifications.

It is suggested that test specifications for handling and containment of polymeric materials for weight loss determinations be included in the materials specifications in order to simplify directions for films, pastes, foams, powders, etc. Operational procedures, of course, are unaffected by the physical state of the samples.

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III. CHEMICAL AND PHYSICAL QUALIFICATION TESTS FOR EPOXY ADHESIVES

At the request of the JPL Cognizant Engineer, an investigation was made of a series of chemical and physical test procedures which have been recommended for preliminary incorporation into the materials specifications for epoxy adhesives. Materials recently submitted for test were Epons 901, 903, 914, 917, 931 A/B, and 422J (all produced by the Shell Chemical Company) since they represent several different types of epoxy adhesives:

Epon 901:	Two-part structural epoxy adhesive, elevated temperature cure (aromatic amine agent)
Epon 903:	One-part structural epoxy adhesive, elevated temperature cure (--- agent)
Epon 914:	One-part structural epoxy adhesive, elevated temperature cure (dicyandiamide agent)
Epon 917:	One-part powder structural epoxy adhesive, elevated temperature cure (anhydride agent)
Epon 931 A/B:	Two-part structural epoxy adhesive (aromatic amine agent)
Epon 422J:	One-part structural epoxy-phenolic adhesive, glass-tape supported (dicyandiamide agent)

(Epons 911, 924, 929, 934 and 941, also studied during this program, were not subjected to analyses since they were previously found unacceptable for various reasons (vide infra)).

The determination of chemical characteristics includes: epoxy equivalent, filler content, hydrolyzable halide content, nonvolatile content, and amine value. Determination of physical properties includes: infrared spectrum and density. The methods employed and the suggested modifications are described in the following paragraphs. The results of the determinations are presented in Tables II-VII, and the infrared absorbance spectra are given in Figures 4-9; these data will be found at the end of this section.

Epoxy Equivalent

Epoxy equivalent is determined according to the procedure described in ASTM Method D 1652-62T, "Epoxy Content of Epoxy Resins," based on the stoichiometric action of hydrogen bromide with epoxy groups to form bromohydrins:

> A weighed sample is dissolved in chlorobenzene (liquid grade resins) or chloroform: benzene (solid grade resins). The solution is titrated with hydrogen bromide in glacial acetic acid, using crystal violet indicator solution.
>
> Values are computed as grams of resin containing one gram equivalent of epoxy groups.

Hydrolyzable Halide Content

The hydrolysis of an epoxy resin sample is conducted according to the procedure described in ASTM Method D 1726-62T, "Hydrolyzable Chlorine Content of Liquid Epoxy Resins." However, the titration procedure has been modified to provide for direct determination of hydrolyzed halide since consumption of alkali may not necessarily be due entirely to the halide groups:

> A weighed sample is refluxed in an excess of alcoholic potassium hydroxide. The hydrolyzate is neutralized and acidified with 1:1 nitric acid solution and titrated potentiometrically with silver nitrate solution.
>
> Values are reported as weight per cent hydrolyzable halide.

Filler Content

Filler content of adhesive bases is determined according to the Shell Company Method, ADM No. 3.

> Weighed amounts of sample and Celite filter aid are stirred and dispersed in chlorobenzene, then filtered through a sintered glass funnel.
>
> Values are reported as weight per cent filler.

Nonvolatile Content

The nonvolatile content is determined in accordance with the procedure described in ASTM Method D 1259-61, "Nonvolatile Content of Resin Solutions," Method B:

> A weighed sample of resin solution is spread under pressure between two weighed sheets of aluminum or tin foil. The sheets are then pulled apart and the resin is dried at 105 ^{o}C in a forced draft oven for 2 hours.
>
> Values are reported as weight per cent volatile material.

Density

The density of powder resins is determined as described in ASTM Method No. D 1895-61T, "Apparent Density, Bulk Factor, and Pourability of Plastic Materials:"

> Resin powder is poured through a powder funnel into a weighed known-volume measuring cup; cup and contents are re-weighed.

The ASTM Method No. D 1875-61T, "Density of Adhesives in Fluid Form," was suggested for density of the adhesive pastes; however, the physical nature of the epoxy resins created difficulties in handling such as loading the cups, eliminating air pockets, etc. Therefore, the simpler method of water displacement was employed.

Values for density are reported as grams per cubic centimeter.

Infrared Spectrum

The infrared absorbance spectra of the epoxy adhesives were prepared in the following fashion:

> The resin is separated from filler by dispersion of the sample in acetone; the filler-free solution is evaporated to a very low level and then placed on a sodium chloride plate and the remainder of acetone evaporated under an infrared lamp. A second salt plate is pressed over the sample to form a clear, uniform film of resin, and then the infrared spectrum is obtained from 2 to 15 microns. (A Perkin-Elmer Model 221 was used for the spectra illustrated in this Section.)

TABLE II

EPON 901*: DETERMINATIONS OF CHEMICAL AND PHYSICAL PROPERTIES

Material	Property	Values
Adhesive Base	Epoxy Equivalent	356
	Hydrolyzable Halide Content	0.083-0.092%
	Filler Content	43.65-43.68%
Curing Agent B-3	Hydrolyzable Halide Content	0.017%
	Amine Value	(in progress)

*Shell Chemical Company

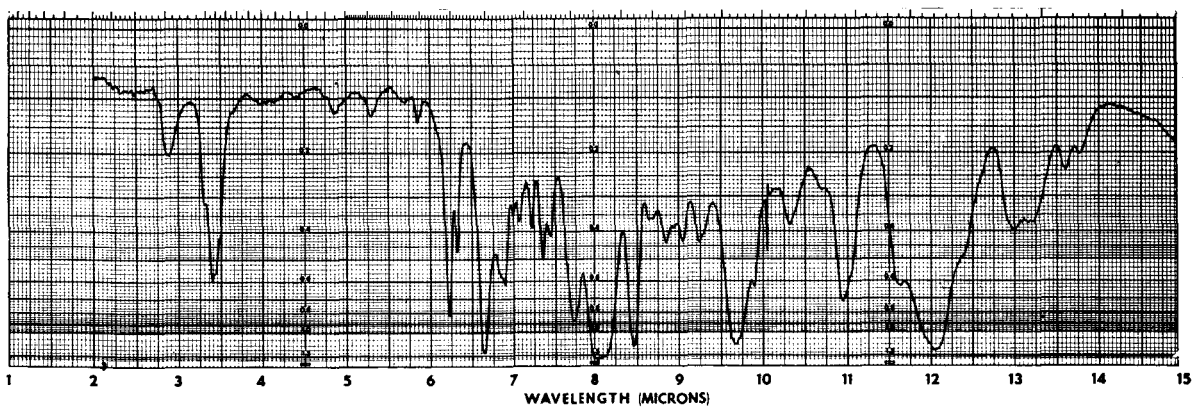


FIG. 4 INFRARED ABSORBANCE SPECTRUM OF EPON 901

TABLE III

EPON 903*: DETERMINATIONS OF CHEMICAL AND PHYSICAL PROPERTIES

Material	Property	Values
Adhesive	Epoxy Equivalent	365-367
	Hydrolyzable Halide Content	0.034-0.045
	Filler Content	45.47-45.48%
	Nonvolatile Content	99.78-99.81%
	Density	1.44 g/cc

*Shell Chemical Company

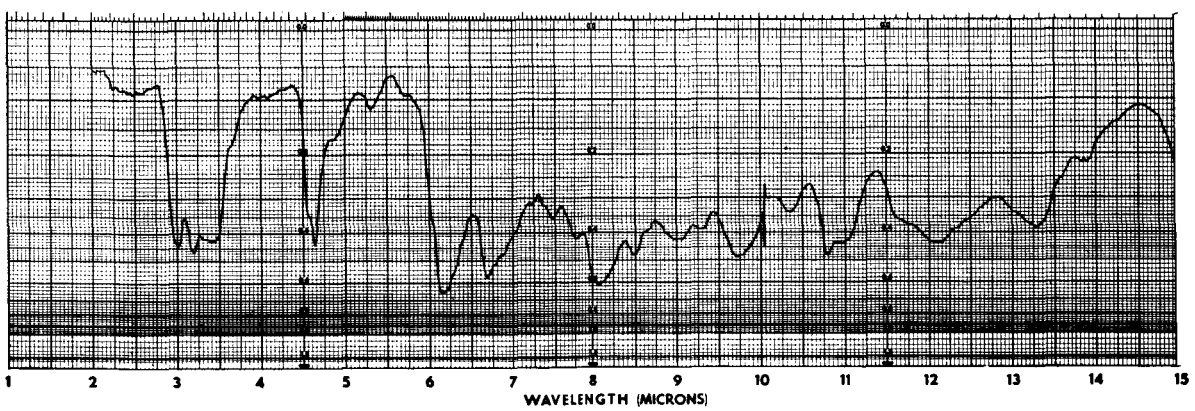


FIG. 5 INFRARED ABSORBANCE SPECTRUM OF EPON 903

TABLE IV

EPON 914*: DETERMINATIONS OF CHEMICAL AND PHYSICAL PROPERTIES

Material	Property	Values
Adhesive	Epoxy Equivalent	257-257
	Hydrolyzable Halide Content	0.105-0.112%
	Filler Content	30.45-30.45%
	Nonvolatile Content	99.77-99.82%
	Density	1.09 g/cc
	Amine Value	(in progress)

*Shell Chemical Company

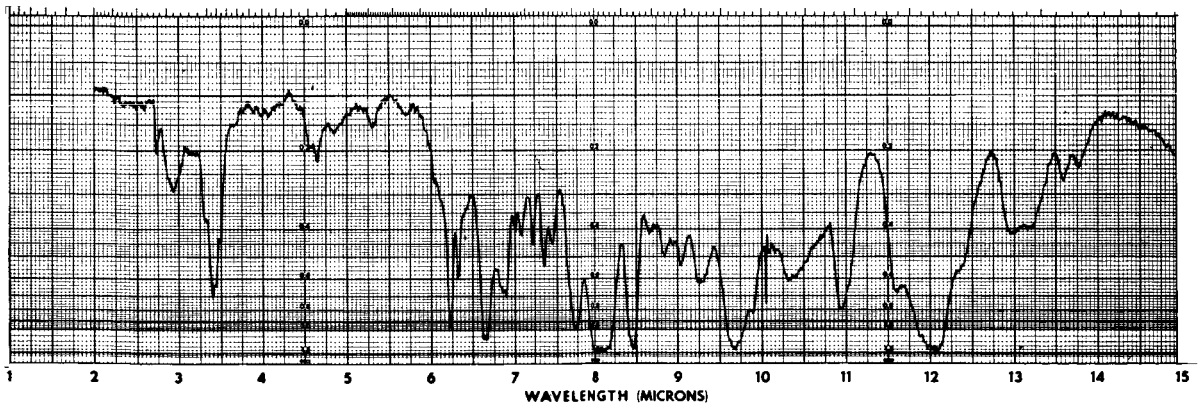


FIG. 6 INFRARED ABSORBANCE SPECTRUM OF EPON 914

TABLE V

EPON 917*: DETERMINATIONS OF CHEMICAL AND PHYSICAL PROPERTIES

Material	Property	Values
Adhesive	Epoxy Equivalent	349-350
	Hydrolyzable Halide Content	0.007%
	Filler Content	20.57-20.89
	Nonvolatile Content	99.85-99.89%
	Density	1.68 g/cc

*Shell Chemical Company

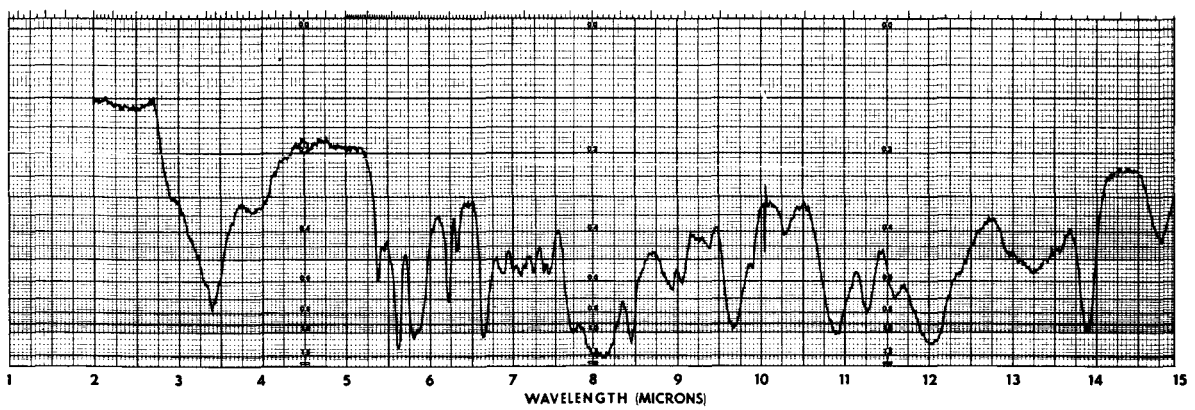


FIG. 7 INFRARED ABSORBANCE SPECTRUM OF EPON 917

TABLE VI

EPON 931 A/B*: DETERMINATIONS OF CHEMICAL AND PHYSICAL PROPERTIES

Material	Property	Values
Adhesive Base	Epoxy Equivalent	167-169
	Hydrolyzable Halide Content	0.092-0.124%
	Filler Content	31.25-31.28%
	Nonvolatile Content	99.53-99.55%
	Density	1.29 g/cc
Curing Agent	Amine Value	(in progress)
	Hydrolyzable Halide Content	0.03%
	Nonvolatile Content	98.92-99.58%
	Density	1.04 g/cc

* Shell Chemical Company

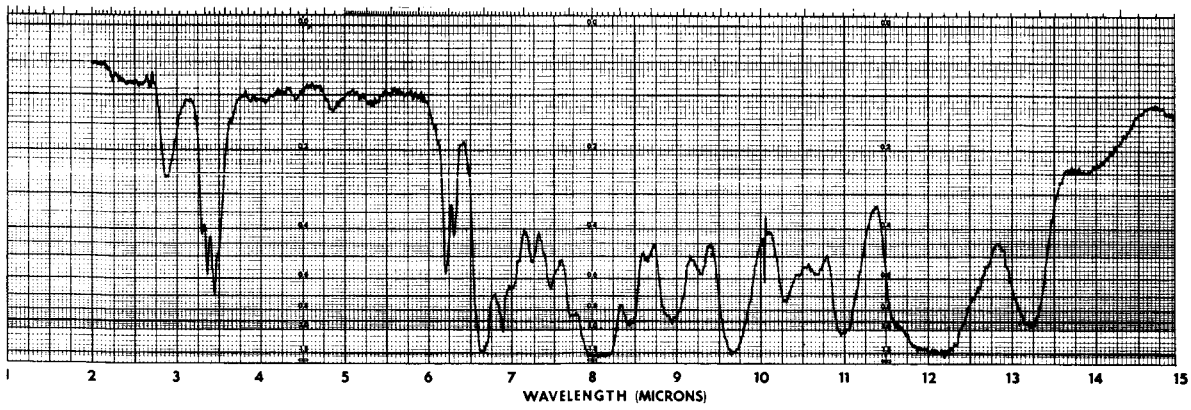


FIG. 8 INFRARED ABSORBANCE SPECTRUM OF EPON 931 A/B

TABLE VII

EPON 422J*: DETERMINATIONS OF CHEMICAL AND PHYSICAL PROPERTIES

Material	Property	Values
Adhesive	Epoxy Equivalent	(in progress)
	Hydrolyzable Halide Content	0.051-0.058%
	Filler Content (Tape)	93.3-93.8%
	Nonvolatile Content	97.05-97.10%
	Resin Content	0.022 g/in^2
	Amine Value	(in progress)

*Shell Chemical Company

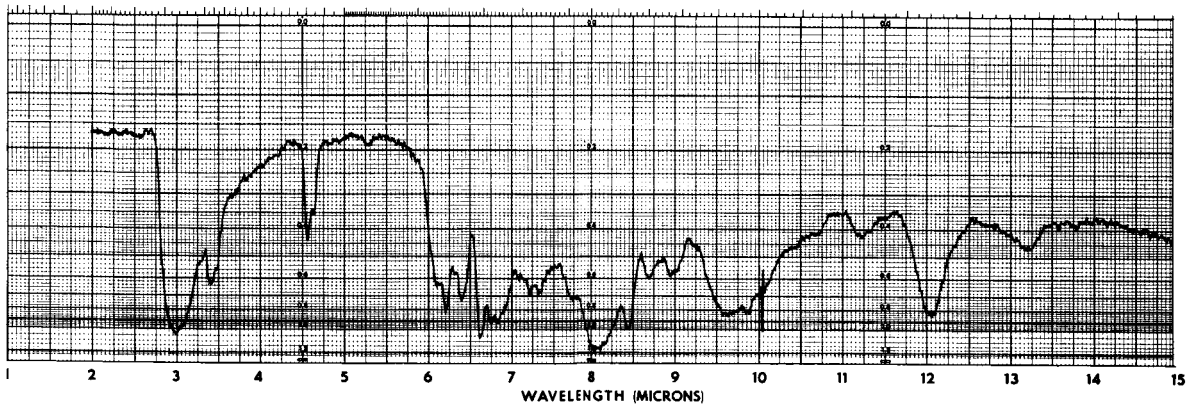


FIG. 9 INFRARED ABSORBANCE SPECTRUM OF EPON 422J

IV. WEIGHT-LOSS BEHAVIOR OF SELECTED POLYMERIC MATERIALS IN A VACUUM-THERMAL ENVIRONMENT

A. PROCEDURES

Exploratory work was performed on the weight-loss behavior of three classes of polymeric materials which were selected for preliminary screening by the JPL Cognizant Engineer. These classes of materials were:

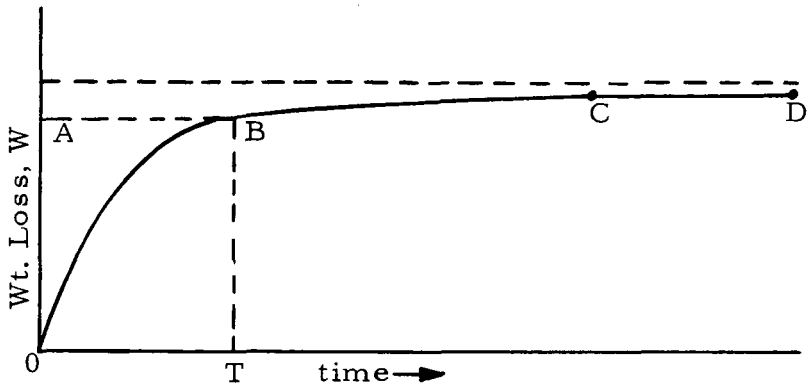
(1) Epoxy adhesives
(2) Silicone rubbers
(3) Polyfluorocarbon films.

The materials were maintained in a vacuum for 80 to 200 hours at 150 ^{o}C and 200 ^{o}C. The lower temperature (150 ^{o}C) was selected because of its similarity to the temperatures proposed for heat sterilization (in inert atmosphere) of spacecraft components; the higher temperature was included in this study in order to gain insight into the stability of the epoxide polymers in the region of temperatures where decomposition of most organic materials is known to take place.

Loss-of-weight was determined for the various polymers, and analysis was made of released material in order to determine origin, e. g., polymer chain degradation, additives, etc. The original polymeric materials were characterized by spectroscopic techniques.

The effect of material purity, curing processes, and sample thickness on weight loss was investigated for some of the epoxy adhesives and silicone rubbers.

The weight-loss of polymeric materials in a vacuum is dependent on temperature, the amount and kind of extraneous material present, and the geometry of the sample. The rate of loss of material, in general, has been found to follow the asymptotic curve illustrated on the following page:



The slope of the curve in the region B to C is found to be so small that it appears to be a straight line and, indeed, if there are errors in the weight-loss values and if the time interval between B and C is only of the order of several hundred hours, even a least squares analysis of the data may suggest a straight line. Since the point C on such a curve represents at least 98% of the total weight loss which can be incurred by a thermally-stable polymer, and this value can be achieved within time spans conveniently of the order of several hundred hours, the hypothetical straight line drawn between points B and C can be used to characterize polymers for their applicability in the construction of space vehicles. The point B is also arbitrarily selected; it is established by inspecting a plot of weight-loss data points and determining when the pronounced initial curvature of the plotted line appears to blend into the "straight" portion of the line.

As has been indicated above, this overly-simplified treatment of weight-loss data is useful for characterization of polymers; in accordance with work reported by others, * and in keeping with the

*Fulk, M. M., and Horr, K. S., "Sublimation of Some Polymeric Materials in Vacuum," Ball Brothers Research Corporation, TN 62-118, 10 September, 1962.

data presented in this Section of the report, point A in the above Figure is called the "initial weight loss," "T" is the time required to achieve a steady-state loss rate, and the steady-state loss rate ($\frac{\Delta W}{\Delta T}$) is computed from the line BC.

The slope of the line BC and its apparent linearity should not be taken as indication that the polymeric substance is decomposing at a steady rate. To be sure, certain polymers may actually decompose and, in these instances, the "straight-line" portion of the weight-loss data implies that a considerable portion of the polymer will disappear on prolonged heating. For thermally-stable, useful polymers, the slope of the line BC represents a nearly-steady rate of evolution of materials; after prolonged heating in a vacuum, the slope of the line gradually decreases and, as indicated in the above figure, the line CD now represents a new "steady-state" evolution of material. It is intuitively obvious that if the weight-loss determination covers a sufficient period of time, it may be nearly impossible to determine the final rate at which a polymer is releasing materials. The best method for determining the rate at which a polymer releases small quantities of materials and whether these materials represent decomposition products involves the direct introduction of the polymer in a specially-constructed mass spectrometer inlet system.

It is obvious that the "weight-loss" of a polymer is a variable number; hence, all "weight-loss" values must include the time of the determination, the geometry of the sample, and temperature (it is assumed that the vacuum conditions are sufficient so as not to impede the egress of materials from polymer surfaces).

Apparatus

The vacuum apparatus used in these studies is illustrated in Figure 10. A mercury diffusion pump was utilized to attain a pressure of 10^{-6} torr in the primary manifold; pressure was measured via a Phillips ionization gage (Consolidated Vacuum Corporation). The polymeric samples were confined in modified resin flasks (Figure 11)

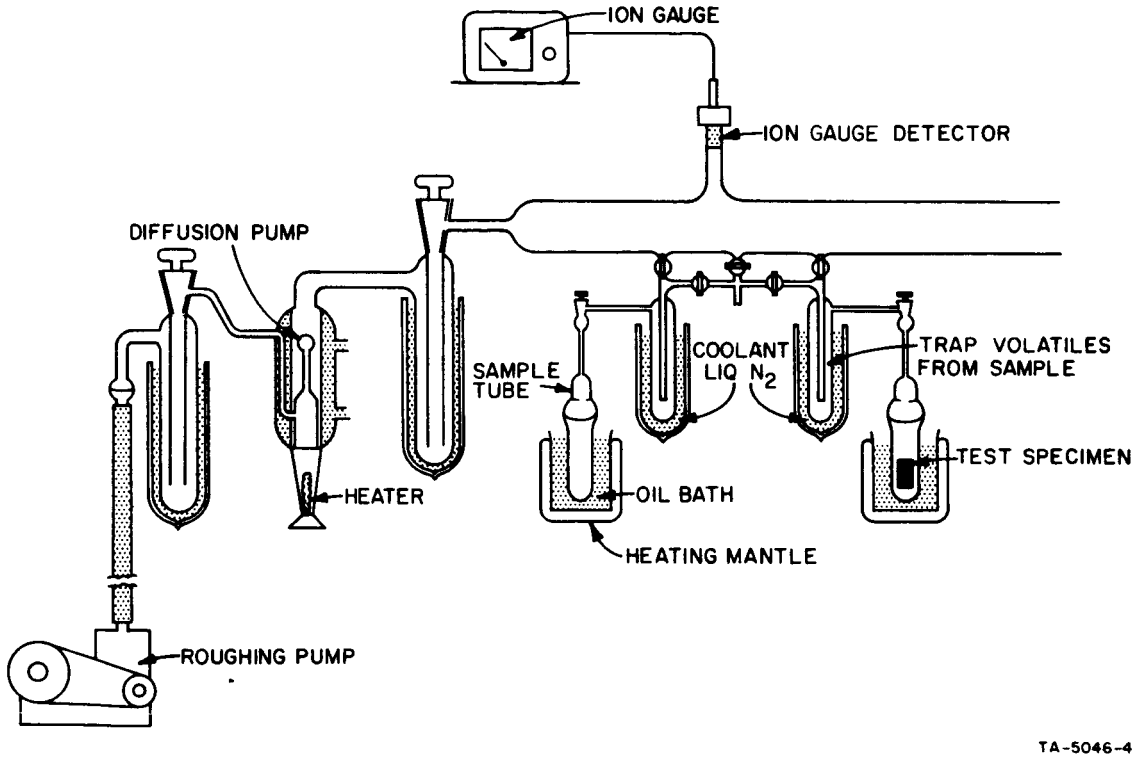


FIG. 10 APPARATUS FOR THERMAL-VACUUM TREATMENT OF POLYMERIC MATERIALS

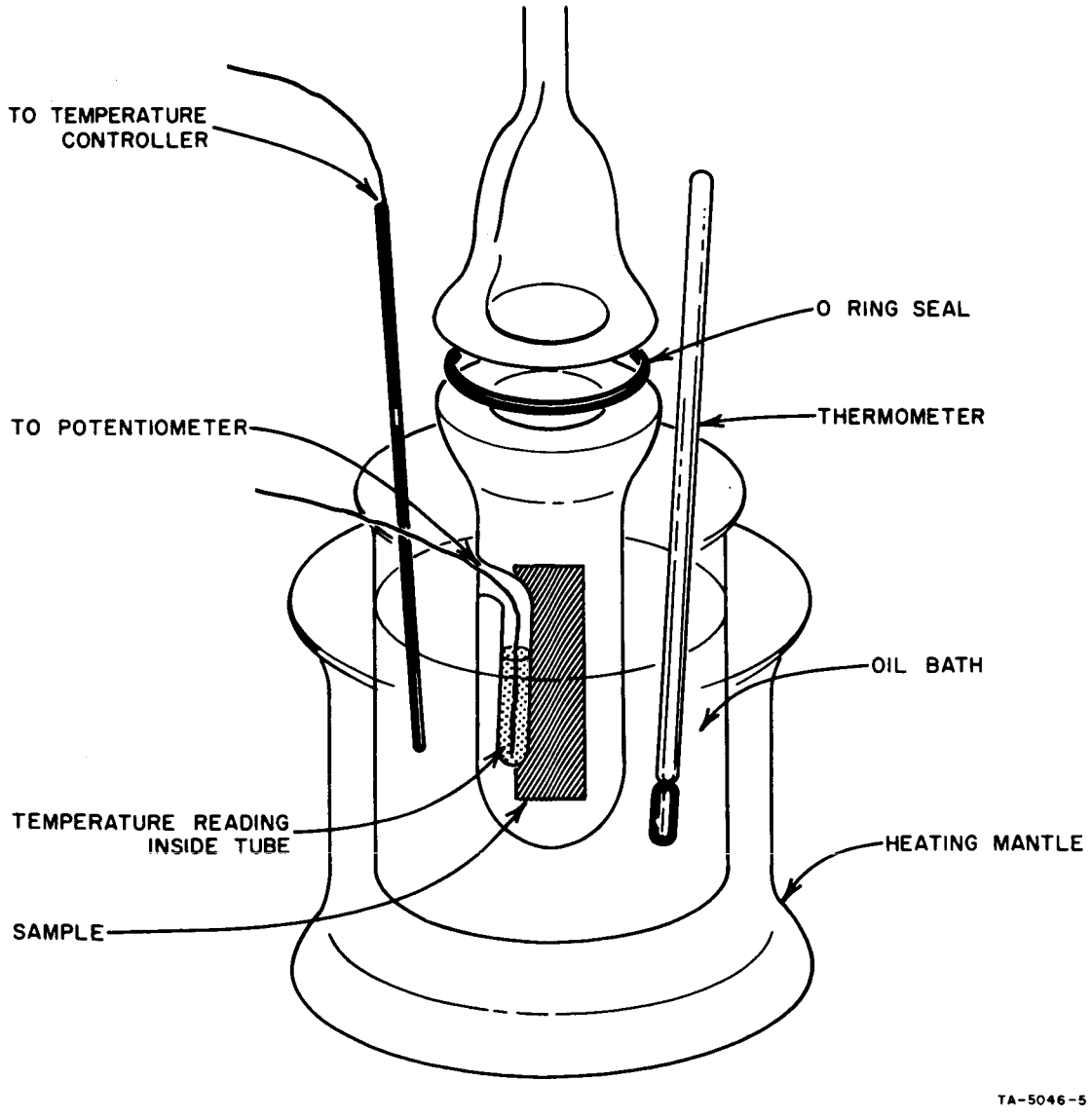


FIG. 11 DETAILED DRAWING OF SAMPLE CELL ASSEMBLY

which were immersed in silicone-oil baths (Dow-Corning No. 550) contained in stainless steel beakers equipped with heating mantles. The temperature of the oil baths was regulated by "Thermistemp" controllers and power was furnished by variable transformers; thermometers were used to monitor the bath temperature. Temperature in the sample cells was measured by thermocouples inserted in wells.

Each sample cell was isolated from the primary manifold by a liquid nitrogen trap. The system was arranged so that gaseous materials condensed at liquid nitrogen temperature could be volatilized at room temperature and transferred into gas sample flasks for analysis.

General Procedure

Sample preparation, size, and geometry varied with the class of polymer and will be discussed in the appropriate parts of the Section.

The samples were removed periodically from the sample cells for weighing ($\pm$0.05 mgm), generally about every 24 hours, and then returned to the cells and immediately brought under vacuum. Although the superiority of continual weighing under vacuum is recognized, it was felt that this procedure could serve as a rapid screening method for polymeric materials in lieu of expensive thermogravimetric equipment.

At the termination of the total exposure period, the gases condensed in liquid nitrogen traps were analyzed with a mass spectrometer (Consolidated Electrodynamics Corporation Model 21-103C). In the instances where a sufficient amount of material condensed on the cooler surfaces of the resin flasks, the condensate was removed for analysis by infrared spectroscopy (Perkin Elmer Model 221). Ultraviolet-visible spectra were obtained for some films (Cary Model 14).

The samples were examined at each withdrawal for alteration of color or other changes in physical properties, and the cells were examined for the presence of condensed materials.

B. EPOXY ADHESIVES

The "Epon" series of adhesives manufactured by the Shell Chemical Company are representative of the epoxy adhesives which have been used for both structural and nonstructural applications in spacecrafts. A series of 11 Epons was suggested for preliminary work on outgassing characteristics, but subsequent discussion with JPL and the Shell Company resulted in the elimination for space use of Epon 911 which contains a polysulfide, and Epons 941 and 929 for which good quality control standards have not been established. (Preliminary screening of Epon 941 indicated properties similar to the other adhesives, but extensive work was not undertaken.)

Epons 901-B3, 903, 914, 916, 924, 931, 934, and 422J were received as materials of purer fractions than standard production materials. All were refrigerated immediately upon receipt to minimize the unfavorable side reactions which occur at temperatures above $0^{\circ}C$; for example, Epon 422J has a storage life of only two days at room temperature. Table VIII describes further the Epon adhesives selected for study, and a brief discussion of the chemistry of epoxy resins is given in Appendix A.

Preparation of Test Samples

Test samples of the resin were cast on specially-prepared rectangular aluminum strips (Alclad 2024 T-3), 2.7 cm wide and 11 cm long. Initially, 2-mil aluminum sheet was used, but 11-mil aluminum sheet was found to be more satisfactory because the thicker sheets were not curled by the resins during the thermal-vacuum treatments.

The aluminum strips were prepared for bonding by vapor degreasing with trichloroethylene and then etching with chromate solution (2:7:17 parts by weight $Na_2Cr_2O_7$: conc. H_2SO_4: H_2O) at $66 \pm 3^{\circ}C$ for 10 minutes. The strips were rinsed thoroughly with distilled water and dried for 2 hours at $60^{\circ}C$.

TABLE VIII

SHELL EPON ADHESIVES
USED IN WEIGHT LOSS STUDIES

Epon No.	Description
901-B3	Two-part adhesive: (A) a gray thixotropic paste identified as Epon 828 with a metallic filler; (B) a dark-colored liquid curing agent identified[1] as an aromatic amine mixture.
903	A one-part adhesive in the form of a viscous gray paste. Identified[1] as based on Epon 828 and containing an unidentified catalyst and a mixed metallic-inorganic filler.
914	A one-part dark-gray thixotropic paste, reported stable indefinitely at room temperature. Identified[1] as based on Epon 828 with a dicyandiamide curing agent and metallic filler.
917	A one-part adhesive based on an epoxy-anhydride system with a metallic filler. It is a free-flowing powder which melts at about 49°C (120°F) and does not resolidify on cooling.[2]
924	Pipe joint sealer and adhesive compound. Composition not identified.
931	A two-part adhesive: (A) a gray-black paste based on a novel epoxy system[1] other than the diglycidyl ether of Bisphenol A[3]; (B) a red liquid curing agent identified as an aromatic amine.
934	A room temperature curing two-part adhesive which meets the MIL-A-5090D, Type I requirements. Consists of a gray epoxy paste similar to that used in Epon 931[1] and an amber amine curing agent identified[1] as a polyamide. The filler is metallic.
941	Similar to 934, but has poorer quality control.
422J	A gray tape-type adhesive meeting the MIL-A-5090D, Type III, class F requirements. A blend of epoxy and phenolic resins containing a metallic filler and dicyandiamide as curing agent. This blend is applied to 112-Volan A glass fabric support. The adhesive cures with evolution of volatiles to form a porous bond.

[1] Identification by infrared spectra and comparison with known sample.

[2] The Epon 917 adhesive should not be accepted in any form but that of a free-flowing powder.

[3] Epon 828 system is based on the diglycidyl ether of Bisphenol A.

A strip of masking tape was placed across the top of the aluminum strip before spreading the adhesive; the tape was then peeled away to leave a resin-free area for ease of handling. Although the dimensions of the samples are not critical, the surface-area-to-volume ratio was maintained within 5% of that given in the material specifications. The thickness of the test samples varied considerably for the various adhesive systems tested because of the widely differing viscosities of each system.

In the preparation of the two-part adhesives, care was taken to ensure mixing of the two components. (Batches smaller than those recommended by the manufacturer were not prepared in order to ensure homogeneity of the mixture and to reduce losses of the more volatile component.) Mixing was performed manually, using a spatula, according to Shell Company instruction, i. e., vigorous stirring for at least 5 minutes, frequently scraping the spatula and the sides of the container. Detailed preparation of the test specimens is given below.

Epon 901-B3: The adhesive mixture was prepared by vigorously mixing with a spatula 11 g of Part B and 100 g of Part A. An even layer of the adhesive mixture, 15-20 mils thick, was applied to the etched aluminum strips using a camel's-hair brush. The samples were placed in a forced-draft oven at 115°C for 30 minutes; the temperature of the oven was then raised to 175°C, and the samples cured for an additional 90 minutes. The samples were pretreated for 55 hours at 25°C and 3×10^{-6} torr before use.

Epon 903: An even layer of adhesive, about 5 mils thick, was applied to the etched aluminum strips using a putty knife. The samples were cured for 2 hours in a forced-draft oven at 175°C.

Epon 914: An even layer of adhesive, approximately 30 mils thick, was applied to the etched aluminum strips with a putty knife. The samples were cured in a forced-draft oven at 200°C for 35 minutes.

Epon 917: A thin even layer of the powder was applied to one side of the etched aluminum strip with a camel's-hair brush and the sample warmed in an oven to hold it in place. The resulting layer of adhesive was approximately 15 mils thick. The adhesive was then cured for 60 minutes in a forced-draft oven at 150°C.

Epon 931: The adhesive mixture was prepared by thoroughly mixing 9 g of Part B and 100 g of Part A with a spatula. The mixture was then spread on the etched aluminum strips with a putty knife to give a smooth, even layer approximately 25 mils thick. The samples were then cured in a forced-draft oven at 160°C for 60 minutes.

Epon 934: The adhesive mixture was prepared by thoroughly mixing 33 g of Part B to 100 g of Part A with a spatula. The mixture was then spread on etched aluminum strips, using a putty knife, to give an even layer 15-20 mils thick. The samples were cured at ambient temperature (20-25°C) for 7 days.

Epon 422J: The Epon 422J adhesive film was cut to the desired size, the polyethylene protective sheet removed from one side of the sample and the exposed side placed on an etched aluminum strip. The remaining polyethylene protective sheet was then removed, and the exposed surface covered with a sheet of Teflon, then a pane of glass. Gentle pressure (a 500-g weight) was applied to the samples to prevent air bubbles from forming during the curing. The samples were then cured in a forced-draft oven at 165°C for 30 minutes.

Data on weight, size, and thickness of cured samples used for weight loss studies are summarized in Table IX.

Effect of Exposure at 150°C and 10^{-6} torr

As shown in Figure 12, the Epon adhesives reached a steady-state rate of loss of weight within 24-70 hours of exposure at 150°C and 10^{-6} torr; total weight loss after 200 hours of exposure ranged from 0.5% for Epon 914 to 4.5% for Epon 422J. These weight loss data are summarized in Table X. None of the adhesives exhibited any observable signs of degradation at this temperature, with the possible exception of Epon 934 which darkened slightly in color.

The condensable gases which were collected at liquid nitrogen temperatures were analyzed via mass spectroscopy, and found to consist primarily of carbon dioxide and/or water partially due to the condensation of atmospheric constituents during the evacuation following replacement of samples after each weighing; the results of the analyses are given in Table XII.

Effect of Curing Processes on Weight Loss at 150°C

Data were obtained on the effect of curing processes on the weight loss behavior at 150°C of Epons 917 and 422J; Epon 917 was postcured for 2 hours at 175°C rather than the prescribed one hour at 150°C, and Epon 422J was postcured for 6 hours at 175°C. As shown in the following table, additional treatment has decreased weight loss

TABLE IX

WEIGHT AND DIMENSIONS OF CURED EPOXY SAMPLES USED FOR WEIGHT LOSS STUDIES

Epon No.	Weight, g	Area, cm^2	Av. Thickness Mils
901-B3	1.02582 0.73515	22.0 22.6	15-20
903	0.47728 0.39554	23.8 24.6	5
814	2.15919	23.1	30
917	0.81566 1.09140	24.9 25.2	15
924	0.44333 0.27743	24.8 24.3	5
931	1.86748 1.89393	23.1 25.2	25
934	1.4666 1.4767	23.1 24.3	15-20
941	0.87170 1.12772	24.2 24.6	15-20
422J	0.98980 0.96363	22.3 23.7	5

Effect of Curing Processes on Weight Loss Behavior at 150 °C and 10^{-6} torr		
Epon 917		
	Cured for 60 minutes at 150°C	Cured for 2 hours at 175 °C
Initial Weight Loss, %	1.35	0.80
Weight Loss Rate $g\text{-}cm^{-2}\text{-}hr^{-1} \times 10^{6}$	0.94	0.62
Epon 422J		
	Cured for 30 minutes at 165 °C	Postcured for 6 hours at 175 °C
Initial Weight Loss, %	3.97	0.95
Weight Loss Rate, $g\text{-}cm^{-2}\text{-}hr^{-1} \times 10^{6}$	1.28	0.40

and weight loss rate of Epon 917 by about one-third, and of Epon 422J by a factor of 3-4. Attainment of steady-state rates of loss of weight did not vary significantly, probably because exposure at 150°C provided increased curing.

Effect of Sample Thickness on Weight Loss at 150°C

Because of the differences in the viscosities of the various epoxide adhesives, the thickness of the final bonding layer may vary. Therefore, a correlation between the thickness of an adhesive layer and its thermal-vacuum characteristics is of interest. To determine this correlation, weight-loss data were obtained for four samples of Epon 914 which differed only in the thickness of the adhesive layer on the aluminum strip; these data are summarized in Table XI and illustrated in Figure 13. The percent weight loss decreases as the thickness is increased; this would be expected, because the thicker the sample, the slower the over-all diffusion rate of material to the surface.

Effect of Exposure at 200°C and 10^{-6} torr

During the initial exposure (24 hours) to the 200°C environment the behavior of the Epon samples was similar to their behavior at 150°C. Although there was an increase in the total amount of material lost, the relationship among the Epons remained the same:

% range	150°C	% range	200°C
	901		
0-1.0	914	0-1.75	901
	903		903
	931		914
	422J*		941
	917**		
1.0-1.5	941	1.75-2.75	941
	934		934
	917		917
3.0-4.0	924	4.0-5.0	422J
	422J		924

After this initial 24-hour period, large differences in behavior occurred. The times to achieve steady state increased greatly and some materials appeared to equilibrate only after 80 hours or more. Marked increases in the rates of weight loss were also observed. As shown in Table XIII and illustrated in Figure 14, Epon 934 provides an excellent example of this trend. At 150°C, this adhesive achieved steady state in less than 24 hours and had a loss rate of 1.2×10^{-6} g-cm^{-2}-hr^{-1}. At 200°C, it required over 80 hours to reach a steady state and the rate was 8.2×10^{-6} g-cm^{-2}-hr^{-1}. Also at this temperature a considerable quantity of a viscous brown oil was observed to condense in the head of the resin flask, suggesting degradation of the resin. Epons 914 and 931 also appeared to undergo degradation. Epon 924 and 941 may also degrade slightly at 200°C and the rates at this temperature were found to be considerably larger than observed at 150°C. Time to steady state was not consistent at 200°C, ranging from 20 hours for Epon 924 to as high as 120 hours for Epon 931.

* postcured at 175°C for 2 hrs
**postcured at 175°C for 6 hrs

The behavior of Epon 903 was found somewhat ambiguous: Although it showed a very low initial weight loss, it achieved steady state only after about 60 hours. Its steady state weight loss rate was low ($1.2\ g\ cm^{-2}hr^{-1}$); there was no evidence of oil evolution and the test specimen showed little change of color.

Epons 917 and 422J achieved steady state fairly rapidly, and exhibited low steady state loss rates. They showed no signs of degradation. In fact, the value of $0.8 \times 10^{-6}\ g\ cm^{-2}hr^{-1}$ observed for these materials at 200°C was lower than their respective values of 0.94 and 1.28×10^{-6} at 150°C. It has been found that the large initial weight loss of the Epon 422J can be reduced by postcuring the resin.

In general, plots of the weight losses of the Epon adhesives at 150°C as a function of time closely resemble a desorption type of curve, i.e., a good straight-line relationship is obtained within a short time, generally within 24 hours of treatment. This is not the case at 200°C. Several of the adhesives undergo material degradation within the polymer network, and the diffusion of these degradation products plays an important role in the total outgassing process. When weight loss curves of these materials are plotted on a linear scale, it is difficult to ascertain just when a steady state is reached, and in several instances steady state conditions do not appear to be established; however straight lines can be obtained from logarithmic plots of the data.

In most cases, the amount of degradation material released by the polymers was too small to isolate, but it could be discerned as a dark, oily film deposited around the top of the resin flask. The Epon 934 and 931 adhesives released sufficient amounts of degradation product to enable infrared spectroscopic examination. The materials were similar and showed absorbances characteristic of aromatic esters (5.80, 7.95, and 9.30 microns). The degradation product of Epon 931, however, exhibited an additional sharp band at 6.65 microns and a broadening in the 9- to 10-micron region. The base epoxy materials

of the Epon 934 and 931 are identical, with a polyamide as curing agent for the former and an aromatic amine for the latter. The materials obtained in thermal-vacuum treatment do not correspond to unreacted starting material, but are evidently products of the epoxy resin degradation or degradation of unreacted curing agents.

Mass spectroscopic analysis of the more volatile material collected under liquid nitrogen indicated few species other than carbon dioxide and water, again including atmospheric constituents after each replacement of sample; details of these analyses are given in Table XV.

Effect of Postcuring on Weight Loss of Epon 422J at 200°C

At 150°C, Epon 422J exhibited not only a larger initial loss of weight than the other adhesives but also a larger rate of loss after an induction period. At 200°C, however, this adhesive behaved differently from the others, i. e., although the initial weight loss was similar to that at 150°C (4. 43% in the first 24 hours), the loss of weight levelled off so that the final weight loss at 200°C was only 4. 97% after 189 hours, an increase of only 0. 54% in 145 hours. Additionally, no evolution of oily material was observable; the only product indicative of possible degradation was ammonia (12. 8 mol-% by mass spectrometer analysis).

It is noted in the Epon Adhesives Manual (Shell Chemical Company) that Epon 422J "cures with the evolution of volatiles and thus forms a porous bond..." Therefore, incomplete curing coupled with the high porosity of the material provides a reasonable explanation of the anomalously large amount of volatiles observed and it was anticipated that the weight loss of this resin could be greatly improved by postcuring the samples at temperatures greater than 150°C.

Samples were postcured in air and under a nitrogen atmosphere (6-48 hrs at 175°C) to see if any oxidative effects would be observed. On testing these samples, it was found that they behaved identically under thermal-vacuum exposure, yielding weight loss

curves that were indistinguishable within experimental error (Figure 15). Both showed a marked reduction in weight loss over the untreated sample; for example, after 160 hours, the postcured samples had lost only 1.7% of their original weight, compared with 5.0% for the untreated sample. Mass spectroscopic analysis of gases collected under liquid nitrogen indicated only 3.4 mol-% ammonia from the nitrogen-postcured sample and none from the air-postcured sample.

Since postcuring improved the thermal-vacuum characteristics of the Epon 422J material at 200 °C, it was of interest to determine the shortest postcuring time which leads to the minimum weight loss for these sample materials. The data are plotted in Figure 16. Although a 48-hour postcure gave the best results, postcuring periods as short as 6 hours at 175 °C seem sufficient to improve the vacuum outgassing characteristics of this resin and to make it superior in performance at 200 °C to the other adhesives. In addition, in these studies postcuring in air appeared to be as satisfactory as postcuring in a nitrogen atmosphere, and perhaps even preferable in view of the elimination of NH_3 from the outgassing products (the effect of oxidation by small amounts of oxygen in nitrogen gas has not been investigated). Although no testing of the postcured samples were made at 150 °C, it is reasonable to assume that the effects would be similar and might reduce the rather large steady state loss rate observed at this temperature. This steady state loss rate appears to be temperature-sensitive and the amount of material lost seems to have a limiting value, in contrast to materials like Epon 934 or 914 which suggest that they can lose weight indefinitely.

Effect of Component Purity on Weight Loss at 200 °C

The purity of the epoxy resin has been of major concern in most industrial specifications. However, little attention has been given to the effect of the purity of the amine curing agent on the properties of the epoxide resin. It has been observed that amine

curing agents oxidize and that they can absorb carbon dioxide on storage. Therefore, it was of interest to determine the effect of amine purity on the weight loss behavior of epoxide resins and, accordingly, a series of modified resin samples were prepared from combinations of pure and impure curing agent and base epoxy resin.

The diglycidyl ether of "Bisphenol A" was selected as an experimental resin base since it was available in high purity as well as in the form of a commercial grade (impure). The "impure" or commercial grade material, Epon 828, is a clear liquid of low viscosity; in contrast, the "pure" grade Epon X-22 lot 1-62 was a white, crystalline powder. A typical aromatic amine curing agent, m-phenylene diamine, was obtained as a commercial material, m. p. 62-64 ^{o}C (Matheson, Coleman and Bell), and prepared in its pure form by sublimation at 60 ^{o}C/0. 1 mm Hg. The sublimed material was a white crystalline solid, and it was stored under nitrogen atmosphere until use.

Samples for thermal-vacuum testing were prepared by mixing 1. 54 g of the amine curing agent with 10. 0 g of the resin base; and all four possible combinations, i. e., pure resin and pure amine, pure resin and impure amine, impure resin and pure amine, and impure resin and impure amine were prepared. Because of the poor wetting properties of these unfilled adhesive mixtures, they were cast into aluminum foil cups about 3 cm in diameter and about 0. 15 cm deep, rather than on the etched aluminum strips. The cups were lubricated with silicone grease to facilitate removal of the samples after curing. The samples were cured as follows: initial gelation for 4 hours at 55 ^{o}C followed by 2 hours at 120 ^{o}C and then 2 hours at 175 ^{o}C. After cure, the samples were removed from the aluminum foil cups and wiped with acetone to remove any residual mold lubricant; gross surface irregularities were removed with a scalpel.

Weight loss data for these synthetic epoxide analogs were obtained at 200 ^{o}C and 10^{-6} torr at 24-hr intervals for periods up to 210 hours. (See Table XIV and Figure 18). The similarity of data for the initial weight losses suggest surface effects. The weight-loss rates and the weight loss values at 100 hours reflect the outgassing characteristics of the bulk of the material. It is of interest to note the dramatic effect caused by the purity of the amine, considering that it is present in relatively small amounts ($\approx$ 15%). Apparently, it is important to specify the purity of the curing agent, and the data recorded in Table XIV and Figure 18 suggest that the loss-of-weight characteristics of Epons might be intimately related to the purity and nature of the curing agents supplied by the manufacturer.

TABLE X

WEIGHT LOSS DATA FOR SHELL EPON ADHESIVES
($150^{\circ}C$ and 10^{-6} torr)

Adhesive No.	Sample Thickness, mils	Initial Weight Loss, percent	Weight Loss, $g\text{-}cm^{-2} \times 10^{4}$	Steady State Loss Rate $g\text{-}cm^{-2}\text{-}hr^{-1} \times 10^{6}$
934	15-20	1.18	7.7	1.2
914	30	0.49	4.6	0
931	25	0.61	4.4	0
901-B3	15-20	0.79	2.6	0.003
903	5	0.78	1.6	0.21
917	15	1.35	4.6	0.94
941	15-20	1.10	3.5	0.6
422J	5	3.97	17.1	1.28
924	5	3.18	5.4	1.2

TABLE XI

WEIGHT LOSS DATA FOR EPON 914:
EFFECT OF SAMPLE THICKNESS
($150^{\circ}C$ and 10^{-6} torr)

Sample Thickness, mils	Initial Weight Loss		Steady State Loss Rate $g\text{-}cm^{-2}\text{-}hr^{-1} \times 10^{6}$
	percent	$g\text{-}cm^{2} \times 10^{4}$	
3.83	0.95	2.28	0.04
2.75	1.07	1.82	0.03
1.33	1.26	1.02	0.04
0.34	2.24	0.48	0.04

TABLE XII

SUMMARY OF MASS SPECTROMETRIC ANALYSES OF GASES COLLECTED DURING THERMAL-VACUUM EXPOSURE OF EPON ADHESIVES FOR WEIGHT LOSS STUDIES

(150°C and 10^{-6} torr)

Component \ Epon No	Mol-%							
	903	914	917	924	931	934	941	422J
CO_2	93.5	95.4	93.2	93.3	---	73.0	94.8	92.1
H_2O	3.9	2.6	4.3	3.6	91.3	7.6	3.0	5.0
N_2	1.5	1.6	1.6	---	5.4	12.5	---	1.6
O_2	0.3	0.4	0.4	---	1.1	2.6	---	0.4
CH_3COCH_3	0.3	---	0.2	3.1	1.5	2.0	---	0.7
$C_6H_5CH_3$	---	---	---	2.3	---	2.3	---	---
CH_3OH	---	---	---	---	0.7	---	---	---
C_6H_6	0.4	---	0.2	1.3	---	---	0.1	0.1
CH_2Cl_2	0.1	---	0.1	3.8	3.8	---	---	0.1
C_5 hydro-carbon	---	---	---	---	---	---	2.2	---

TABLE XIII

WEIGHT LOSS DATA FOR SHELL EPON ADHESIVES

($200^{\circ}C$ and 10^{-6} torr)

Adhesive No.	Sample Wt. g	Time to Steady State hours	Initial Weight Loss		Steady State Loss Rate $g\ cm^{-2}\text{-}hr^{-1} \times 10^{6}$
			percent	$g\text{-}cm^{-2} \times 10^{4}$	
934	1.48	80	2.22	16.3	8.6
914	2.04	100	1.84	13.7	9.6
931	1.89	120	2.23	15.2	6.3
901-B3*	1.03	15	0.51	2.7	2.5
903	0.396	70	1.77	2.8	1.2
917	1.09	30	2.70	11.8	0.8
941	1.13	100	2.29	10.5	3.9
422J	0.964	20	4.40	17.9	0.8
924	0.277	20	5.51	5.5	4.8

TABLE XIV

WEIGHT LOSS DATA FOR SYNTHETIC EPOXIDE ANALOGS: EFFECT OF COMPONENT PURITY

($200^{\circ}C$ and 10^{-6} torr)

Resin System		Initial Weight Loss(%)	Weight Loss Rate $g\text{-}cm^{-2}\text{-}hr^{-1} \times 10^{6}$	Weight Loss at 100 Hrs.
Epoxide	Amine			
Impure	Impure	0.5	20.9	2.0%
Pure	Impure	0.3	14.4	1.8
Impure	Pure	0.6	4.0	1.0
Pure	Pure	0.33	3.4	0.66

TABLE XV

SUMMARY OF MASS SPECTROMETRIC ANALYSES OF GASES COLLECTED DURING THERMAL-VACUUM EXPOSURE OF EPON ADHESIVES FOR WEIGHT-LOSS STUDIES ($200^{\circ}C$ and 10^{-6} torr)

Component \ Epon No	Mol-%								
	901-B3	903	914	917	924	931	934	941	422J
CO_2	92.7	0.7	96.5	61.2	64.0	0.4	89.1	76.4	---
H_2O	3.7	99.2	2.5	27.4	28.1	92.3	9.1	19.6	66.3
N_2	2.2	---	---	---	---	---	---	1.5	1.7
O_2	0.4	---	---	---	0.3	---	---	0.4	0.3
CH_3COCH_3	0.8	---	0.3	2.8	3.1	1.2	---	2.1	---
$C_6H_5CH_3$	---	---	0.7	---	---	0.4	1.1	---	---
CH_3OH	---	---	---	---	---	1.6	---	---	---
C_6H_6	0.1	---	0.1	---	0.1	---	0.1	0.1	0.1
Aldehydes	---	---	---	8.6	---	4.1	---	---	---
CH_2Cl_2	0.1	---	---	---	---	---	---	---	---
NH_3	---	---	---	---	---	---	---	---	12.8*

* 3.4 mol-% after postcure in nitrogen, and 0% after postcure in air.

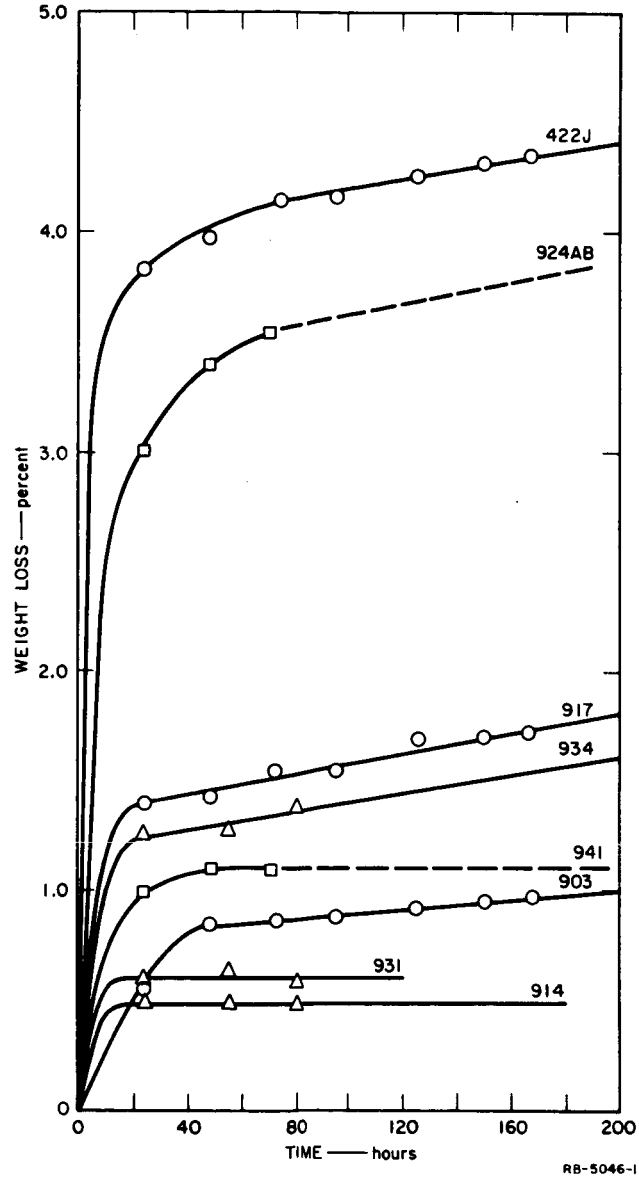


FIG. 12 PERCENT WEIGHT LOSS OF EPON ADHESIVES AT 150 °C AND 10^{-6} torr

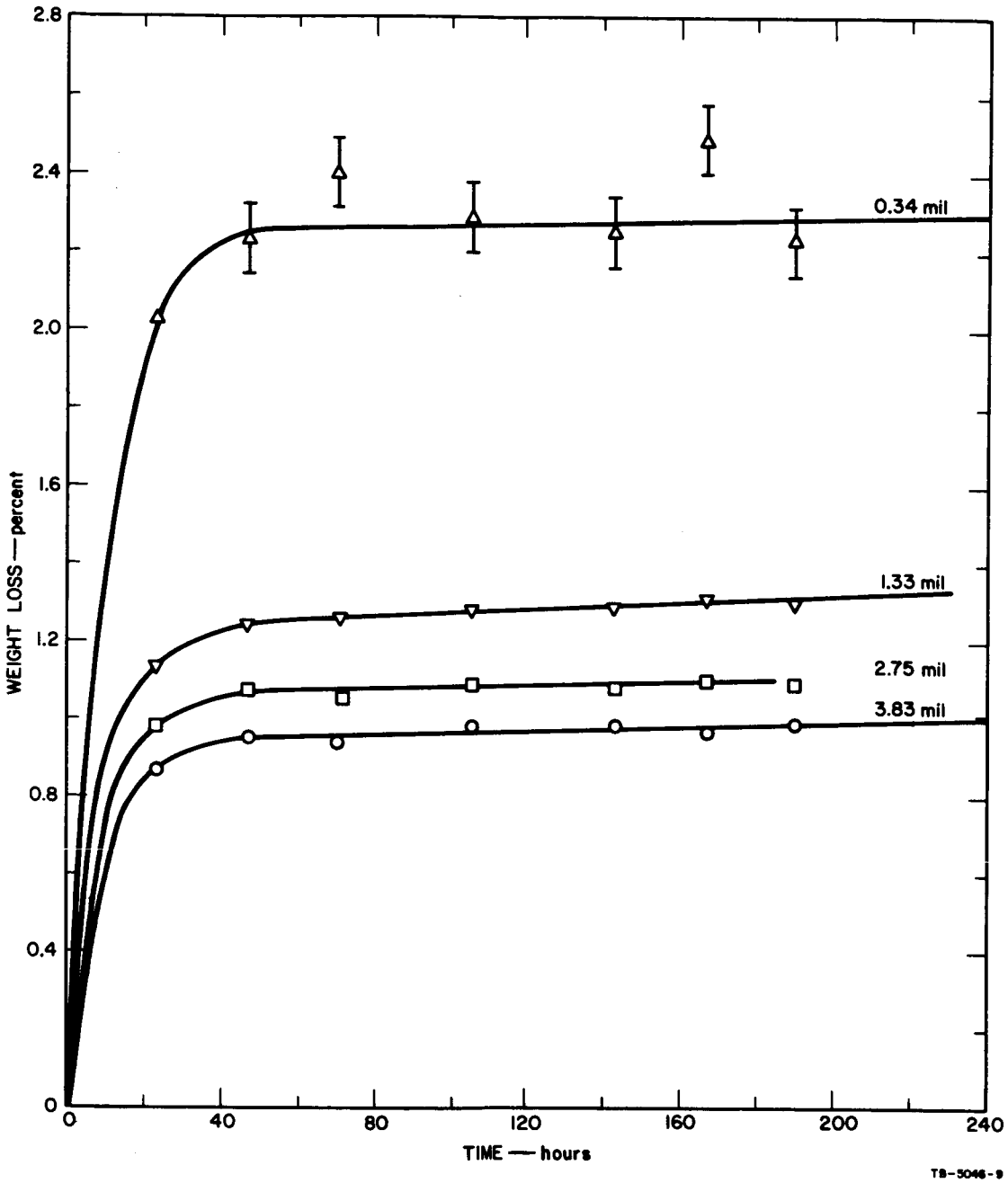


FIG. 13 PERCENT WEIGHT LOSS FOR EPON 914 SAMPLES OF VARIOUS THICKNESSES AT 150 °C AND 10^{-6} torr

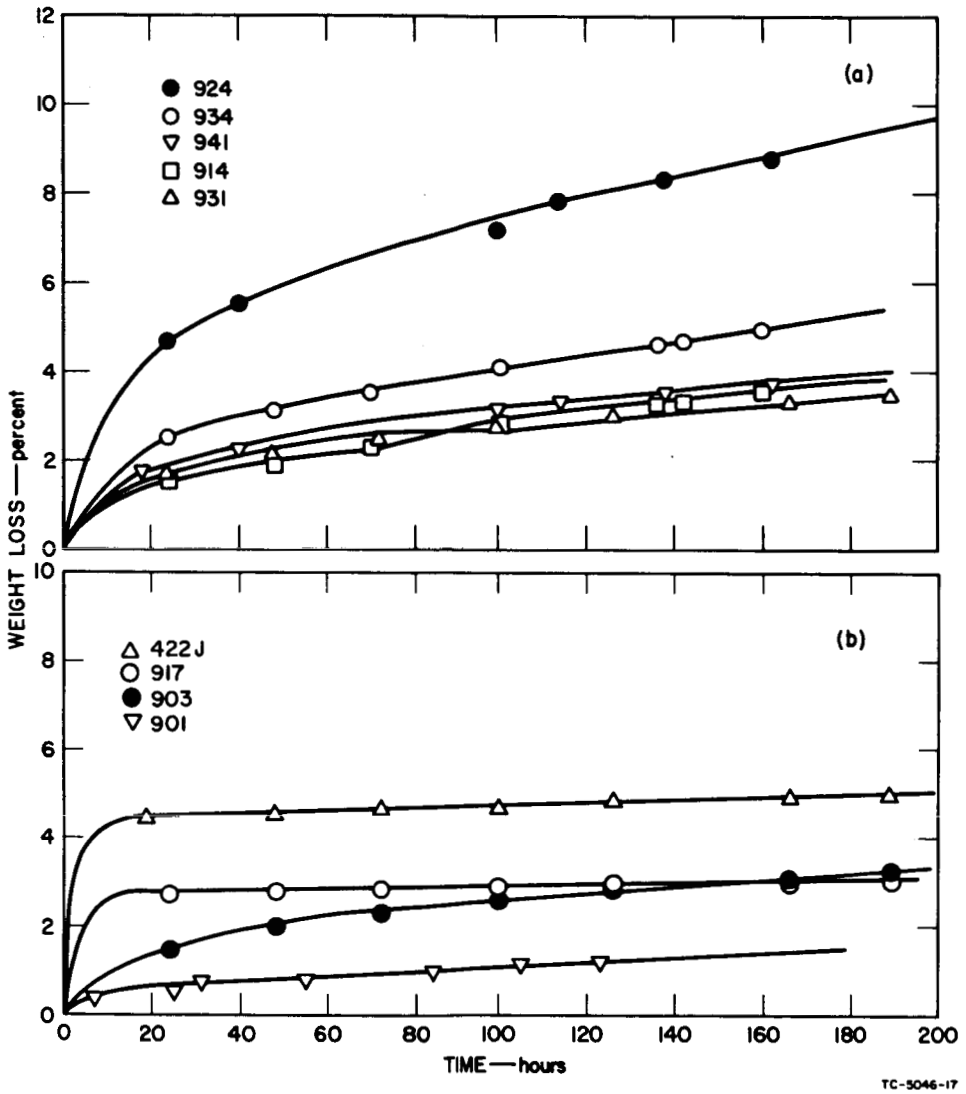


FIG. 14 PERCENT WEIGHT LOSS OF EPON ADHESIVES AT 200 °C AND 10^{-6} torr

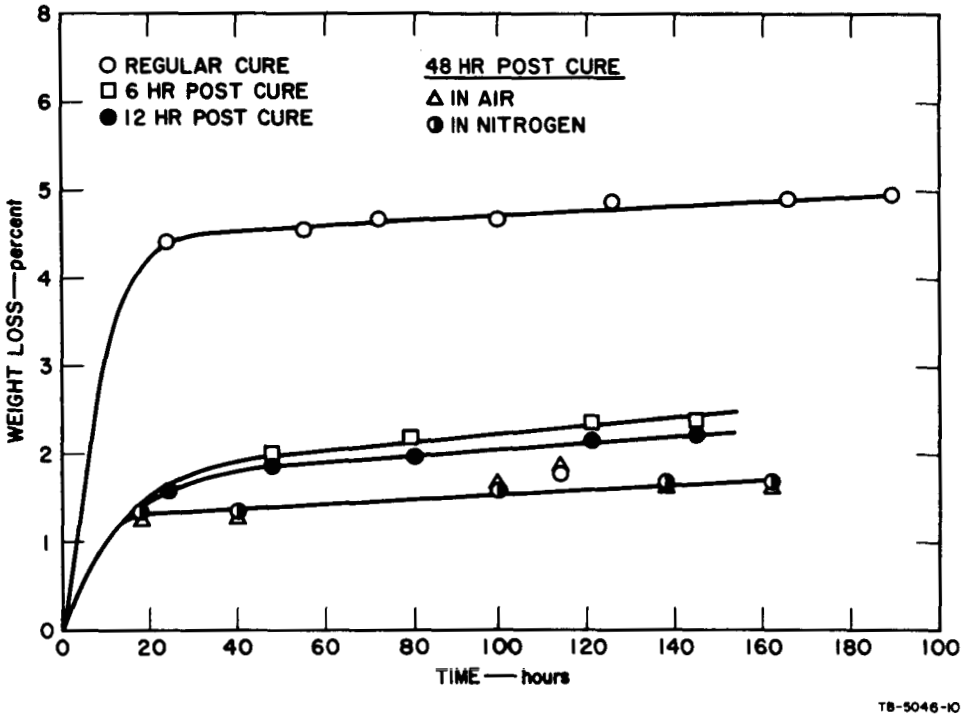


FIG. 15 PERCENT WEIGHT LOSS OF EPON 422J AT 200 °C AND 10^{-6} torr AFTER VARIOUS POSTCURING CONDITIONS

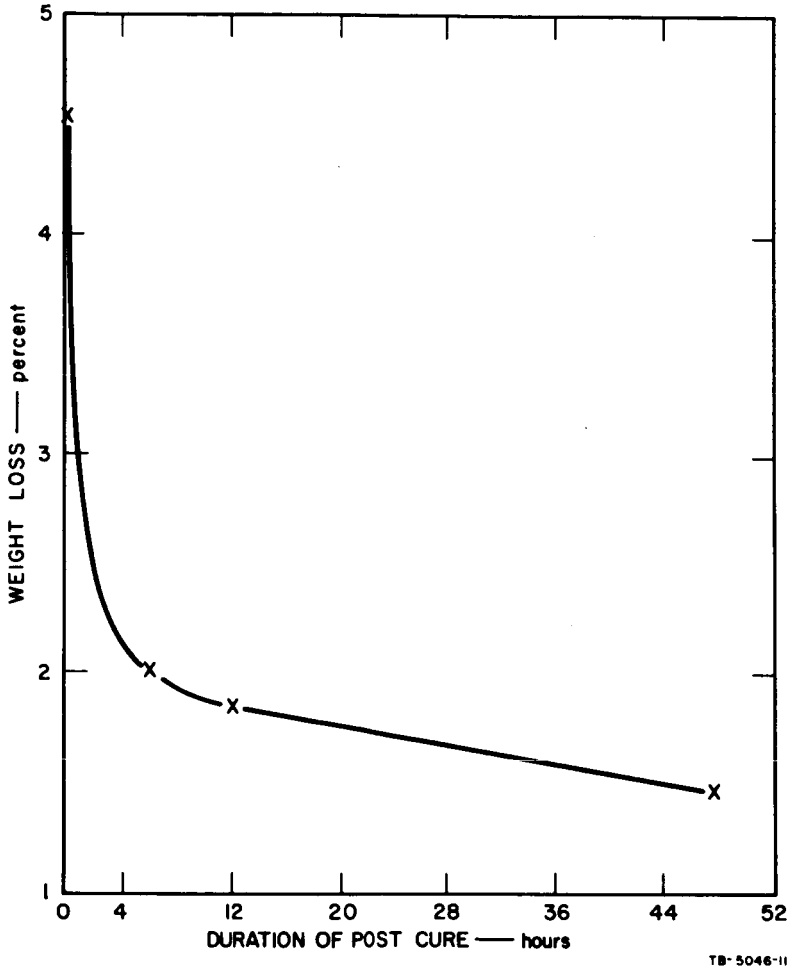


FIG. 16 EFFECT OF VARIOUS POSTCURING TIMES ON WEIGHT LOSS AT 48 HOURS FOR EPON 422J AT 200 °C AND 10^{-6} torr

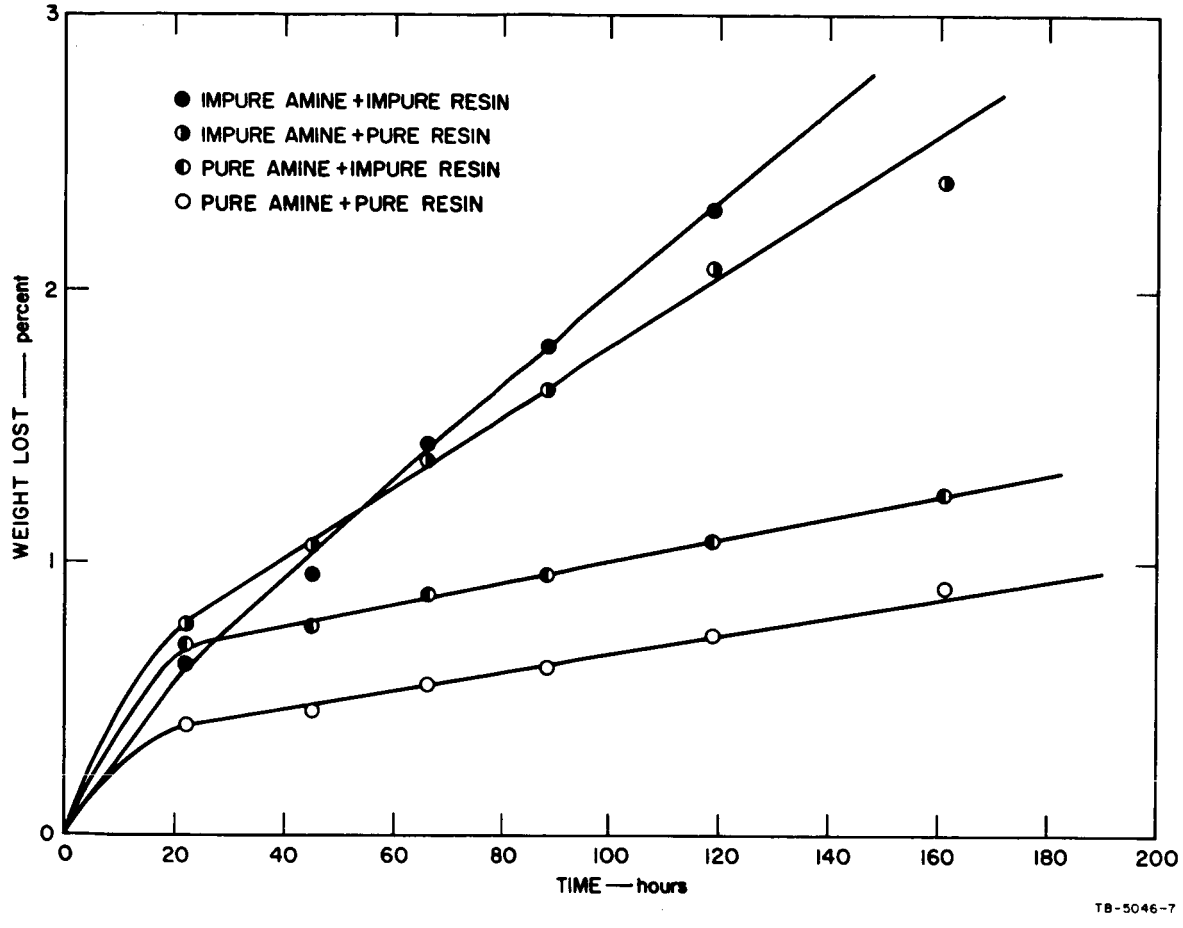


FIG. 17 PERCENT WEIGHT LOSS OF ANALOG RESIN SYSTEMS OF DIFFERENT DEGREES OF PURITY AT 200 °C AND 10^{-6} torr

C. RTV SILICONE POTTING COMPOUNDS AND ADHESIVES

Silicone rubbers are used in the construction of spacecrafts as adhesives and as potting compounds. They are recommended because of their excellent thermal stability; commercial materials in vacuo are stable to approximately 200°C, and it is reported that very pure siloxane polymers may be stable at temperatures as high as 400°C. A brief discussion of the chemistry of silicone polymers is given in Appendix B.

General Electric RTV silicones 11, 60, 511, 560, 615, 102, 106, 108, and 112 were stored under refrigeration immediately upon receipt in order to minimize the side reactions induced by exposure to ambient temperature.

Potting compounds (RTV 11, 60, 511, 560, 615) are liquids or pastes which cure on addition of a catalyst to form the solid rubber. The catalyst used for all potting compounds is dibutyl tin dilaurate, except for RTV-615 which is supplied with its own catalyst. Descriptions of these potting compounds are summarized in Table XVI.

The adhesive/sealants (RTV-102, 106, 108, and 112) are one-package silicone rubbers which cure when brought into contact with atmospheric moisture; no composition data were obtained on these ma materials since they cure rapidly when exposed to air.

Preparation of Samples

Test samples of the silicone potting compounds were cast into shallow cups fabricated from aluminum foil. To ensure uniform sample size, these cups were shaped by a cylindrical glass form 3.0 cm in diameter. The cups were trimmed to a depth of 1/4-inch, and the sides of the cups reinforced with a thin strip of masking tape. Surface areas of the test specimens were calculated on the assumption that they were perfect cylinders.

Test samples of the silicone adhesives were cast directly on strips of 11-mil Alclad 2024-T3 aluminum, 2.7 cm wide and 11 cm long, which had been degreased prior to use by wiping with chloroform.

TABLE XVI

GENERAL ELECTRIC RTV SILICONES USED IN WEIGHT LOSS STUDIES

Silicone	Siloxane Base	Filler	Catalyst
Potting Compounds			
RTV 11	Dimethyl	Silica or TiO_2	T-12*
RTV 60	Dimethyl	Iron Oxide	T-12
RTV 511	Methyl-phenyl	Silica or TiO_2	T-12
RTV 560	Methyl-phenyl	Iron Oxide	T-12
RTV 615	Dimethyl	None	615-B2**
Adhesives***			
RTV 102		White	one-part
RTV 106		Red	one-part
RTV 108		Translucent	one-part
RTV 112		White	one-part

*Thermolite-12, dibutyl tin dilaurate.

**RTV 615 is composed of a part A which is siloxane base and a part B which is a catalyst (a proprietary material supplied by manufacturer).

***Appear to be dimethyl siloxanes.

Surface areas were calculated directly from the measured length and width of the test specimen. Silicone adhesives were cost into cups, so that the data obtained for the adhesives would be comparable with those for the potting compounds.

In general, the silicone potting resin mixtures were prepared in the following manner: The required amount of Thermolite-12 catalyst was added to 10 g of the silicone liquid or paste in a 50-ml beaker and mixed thoroughly with a stainless steel spatula. This mixture was deaerated in a vacuum oven at room temperature. When bubbles no longer formed (generally 15 to 20 min), the mixture was removed from the vacuum oven and poured gently into the aluminum foil cups in such a way so as to avoid air entrapment. The samples were allowed to cure at room temperature for about 1 week before use. Relative humidity was not controlled. Details of sample preparation are given below; weight and dimensions are given, in Table XVII.

RTV 11 and 60 - The silicone mixture was prepared by mixing 10 g of the silicone liquid and 0.01 g (0.1% by weight) of T-12 in a small beaker. After deaeration, the mixture was poured into aluminum foil sample cups and allowed to cure for eight days at room temperature.

RTV 511 and 560 - The silicone mixture was prepared by mixing 10 g of the silicone liquid and 0.02 g (0.2% by weight) T-12 in a small beaker. After deaeration the sample was cured for one week in a desiccator held at room temperature and 50% relative humidity. *

RTV 615 - The silicone mixture was prepared by mixing 10 g of RTV 615 A with 1 g of RTV 615 B. After mixing and deaeration, the material was poured into aluminum cups and cured at room temperature for 7 days.

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* 50% relative humidity was maintained by filling the bottom section of a desiccator with a saturated solution of $Ca(NO_3)_2 \cdot 4\ H_2O$.

TABLE XVII

WEIGHT AND DIMENSIONS OF SILICONE SAMPLES

Silicone	Cured sample weight, g	Sample area, cm^2
Potting Compounds		
RTV 11	5.61986	21.1
RTV 60	6.08525	20.1
RTV 511	4.98969	20.2
RTV 560	6.11943	22.0
RTV 615	5.26418	22.7
Adhesives[3]		
RTV 102	0.46061	19.9
RTV 106	0.29606	20.8
RTV 108	0.40558	20.5
RTV 112	0.57201	20.5

RTV Adhesive/Sealants (102, 106, 108, and 112) - All of these one-part materials were used directly from the tube; they were spread with a spatula onto clean aluminum strips to a thickness of approximately 10 mils and cured for one week at room temperature and 50% relative humidity.

Effect of Exposure at 150°C and 10^{-6} torr for RTV Potting Compounds

All five RTV silicone potting compounds performed poorly under thermal vacuum conditions--large amounts of condensable oils evolved. It is interesting to note that, despite the large weight losses of these materials, none of the samples tested exhibited obvious color changes or alterations in physical properties. The outgassing characteristics of these materials are shown in Figure 18, and summarized in Table XVIII; 40-80 hours were required to achieve a steady state; initial weight losses ranged from 1.6-4.3%, and rates were of the order of 0.1-0.2% per hundred hours.

Effect of Curing Processes on RTV Potting Compounds

The large weight losses observed in our experiments led to the question of whether the potting compounds were completely cured. The samples employed in this study were relatively thick, of the order of 1/4 inch. For samples of 1/4 inch or more in thickness, the manufacturer recommends heating the material to a service temperature of 150°C, to speed cure.* Additionally, only minimum amounts of T-12 catalyst were employed in preparing the mixtures because of their thickness (manufacturer's direction for thick sample). Several of the RTV silicone potting compound test specimens were postcured for 24 hours at 150°C before subjecting them to vacuum-thermal testing; the results are summarized in Table XX. The pretreatment decreased weight losses about 50% (see Table XVIII), but this did not prevent the evolution of rather large amounts of low molecular weight silicone oil.

* GE Technical Data Book, S-38, page 10.

Although small amounts of catalyst were used initially, Thermolite-12 is considered a reliable catalyst and so it was of interest to see if a more complete cure could be obtained by using a larger amount of it. Hence, the catalyst level in several potting compounds was raised from the 0.1-0.2% range to 0.5%. It was found that this increase had virtually no effect on the thermal vacuum behavior of the silicone potting compounds, and so, as corroborated after 48 hours testing, this approach was abandoned.

It was apparent from these postcuring studies that although improved outgassing characteristics were obtained, the release of oils was not eliminated. It was assumed that these oils could not cure into the siloxane network; to assay these assumptions, the resins were exposed to a vacuum postcure of 24 hours at 150°C and 10^{-4} torr. Considerable evolution of oil took place during the first few hours of the thermal vacuum postcure, but this appeared to subside within 24-hours. The samples were allowed to stand in air for three days to re-adsorb surface contaminants so that they would be comparable to the other samples, then they were thermal-vacuum tested in the usual way. This treatment was quite successful, as is shown in Table XXI. Not only were all weight losses greatly reduced, but the volatile condensable oil had been eliminated. Figure 20 shows weight loss curves of RTV 60 for each type of treatment; the thermal-vacuum postcuring appears to be the most effective.

Identification of Condensable Oil from RTV Potting Compounds

As mentioned previously, large amounts of a clear, straw-colored oil were evolved from the silicone potting compounds during testing at 150°C and 10^{-6} mm Hg. Evolution of this oil began when the bath temperature reached 130-140°C and apparently continued for several hours. In the case of RTV 511, enough of this outgassed oil was available for an IR spectrum. This spectrum was identical to that of RTV 511 indicating that the oil is low molecular weight siloxane of similar structure. IR spectra are shown in Figure 21.

It was originally felt that these oils were unreacted silicone fragments and an attempt was made to eliminate them by increasing the catalyst level in the silicone mixtures. As indicated above, this treatment was not effective. Thin film studies were then undertaken, no structural changes could be detected in the infrared spectra of the RTV silicones heated at 150°C under vacuum for several hundred hours; therefore, it was assumed that the oils are not degradation products. It was concluded on the basis of these data that these oils are low-molecular-weight silicones added as plasticizers, viscosity controllers, and/or processing aids. They have the same structure as the silicone polymers.

Effect of Exposure at 150°C and 10^{-6} torr for RTV Adhesive/Sealants

Weight loss data for the adhesive/sealants are given in Table XIX and are plotted in Figure 19. The percent weight losses of these materials are very similar; all had initial weight losses ranging from 5.4-6.0%, and all evolved oils within the first hour of heating.

Recommendations

It is recommended that all the silicone materials treated in this study be subjected to some modification of posttreatment or formulation in order to eliminate low-molecular-weight silicone oils and other substances formed during cross linking (see Appendix B, reactions I and II). Although the vacuum postcuring technique was quite successful in eliminating these from the potting compounds, it is realized that this treatment might not be applicable to many spacecraft assemblies.

TABLE XVIII

WEIGHT LOSS DATA FOR RTV SILICONE POTTING COMPOUNDS

($150^{\circ}C$ and 5×10^{-6} mm Hg)

RTV Silicone	Initial Weight Loss		Weight Loss Rate		Est. time to steady state, hrs
	$g\text{-}cm^{-2} \times 10^{4}$	percent	$g\text{-}cm^{-2}\text{-}hr^{-1} \times 10^{6}$	%/100hr	
511	107	4.33	5.2	0.21	75
560	93.4	3.36	2.7	0.10	35
11	72.5	2.72	4.8	0.18	55
615	44.8	1.93	4.2	0.18	70
60	49.0	1.62	1.7	0.06	55

TABLE XIX

WEIGHT LOSS DATA FOR RTV SILICONE ADHESIVE/SEALANTS

($150^{\circ}C$ and 5×10^{-6} mm Hg)

RTV Silicone	Initial Weight Loss		Weight Loss Rate		Est. time to steady state, hrs
	$g\text{-}cm^{-2} \times 10^{4}$	percent	$g\text{-}cm^{-2}\text{-}hr^{-1} \times 10^{6}$	%/100hr	
112	14.0	6.07	0.1	0.07	100
108	11.8	5.90	0.1	0.11	100
106	7.4	5.42	0.3	0.09	100
102	16.8	5.95	0.1	0.05	100

TABLE XX

WEIGHT LOSS DATA FOR RTV SILICONE POTTING COMPOUNDS POSTCURED IN AIR

($150^{\circ}C$ and 5×10^{-6} mm Hg)

RTV Silicone	Initial Weight Loss		Weight Loss Rate		Est. time to steady state, hrs
	$g\text{-}cm^{-2} \times 10^{4}$	percent	$g\text{-}cm^{-2}\text{-}hr^{-1} \times 10^{6}$	%/100hr	
60	20.7	0.82	0.8	0..04	80
11	26.6	1.21	2.6	0.21	80
560	50.0	1.71	1.0	0.03	95
511	47.1	1.88	2.8	0.16	100

TABLE XXI

WEIGHT LOSS DATA FOR RTV SILICONE POTTING COMPOUNDS POSTCURED IN VACUUM

($150^{\circ}C$ and 5×10^{-6} mm Hg)

RTV Silicone	Initial Weight Loss		Weight Loss Rate	
	$g\text{-}cm^{-2} \times 10^{4}$	percent	$g\text{-}cm^{-2}\text{-}hr^{-1} \times 10^{6}$	%/100hr
60	10.4	0.35	0.0	0.01
560	11.3	0.46	0.2	0.01
11	14.1	0.52	3.3	0.11
615	17.9	0.78	0.8	0.10

TABLE XXII

WEIGHT CHANGES DURING VACUUM POSTCURE CYCLE

RTV Silicone	Original sample wt.	Weight after post-curing	% Wt. Loss	Wt. after 3 days in air	% Wt. Gain	Over-all wt. loss %
615	4.68625	4.61465	1.53	4.61595	0.03	1.50
11	5.68011	5..61990	1..06	5.62569	0.08_5	0.97_5
60	5.65682	5..59112	1.16	5.59573	0.08	1.08
560	4.61445	4.47032	3.12	4.47225	0.06	3.06

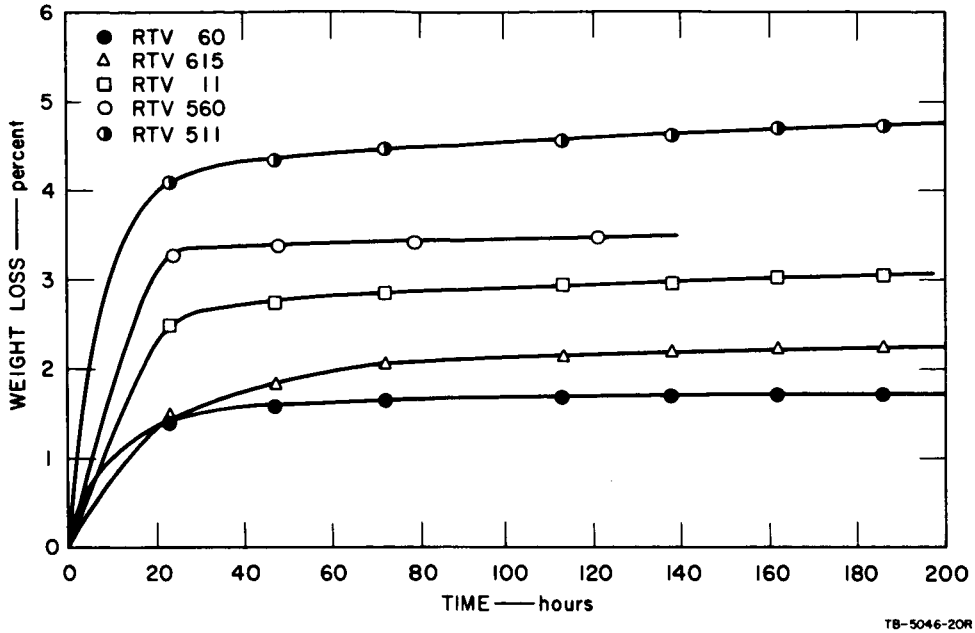

FIG. 18 PERCENT WEIGHT LOSS OF RTV SILICONE POTTING COMPOUNDS AT 150 °C AND 10^{-6} torr

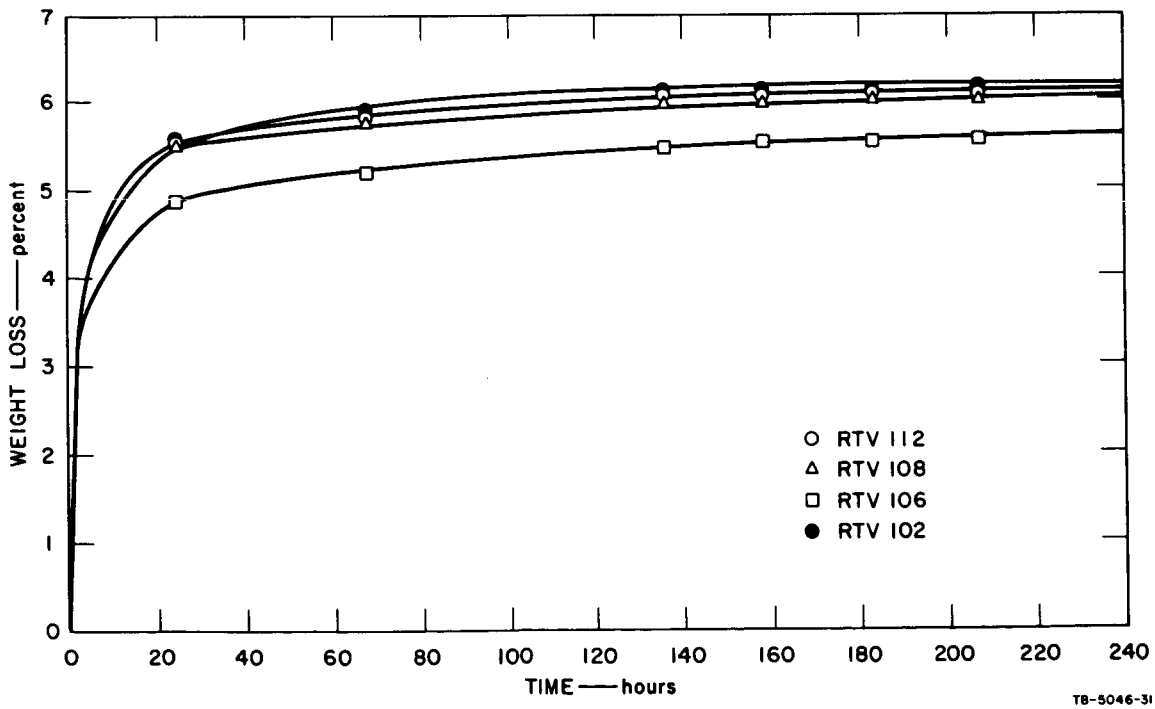

FIG. 19 PERCENT WEIGHT LOSS OF RTV SILICONE ADHESIVE/SEALANTS AT 150 °C AND 10^{-6} torr

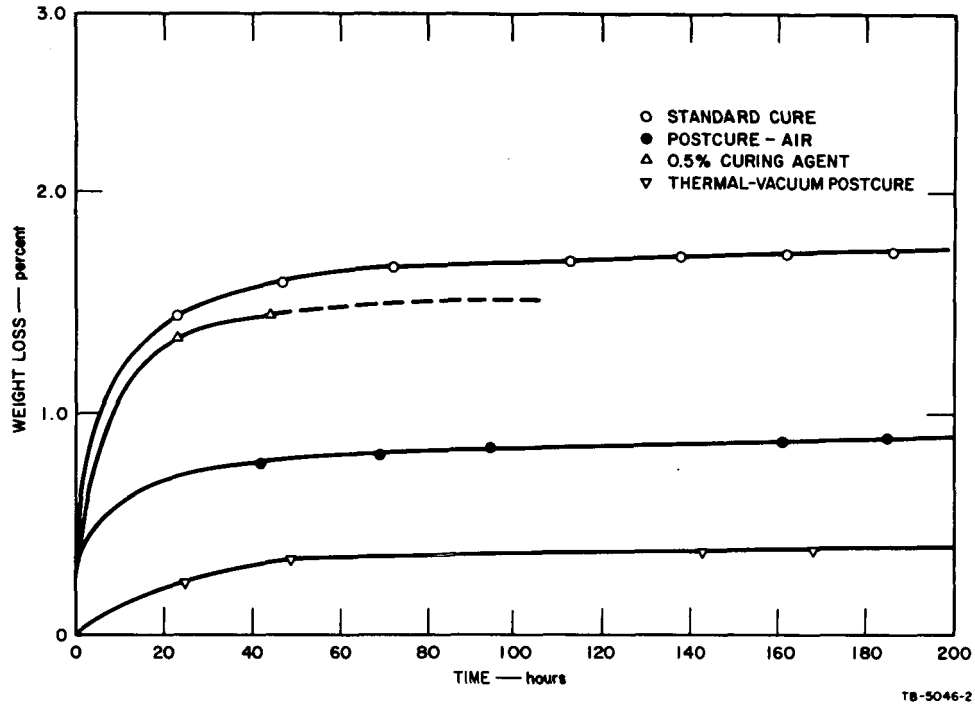

FIG. 20 EFFECT OF VARIOUS PRETREATMENTS ON THE WEIGHT LOSS OF RTV 60 AT 150 °C AND 10^{-6} torr

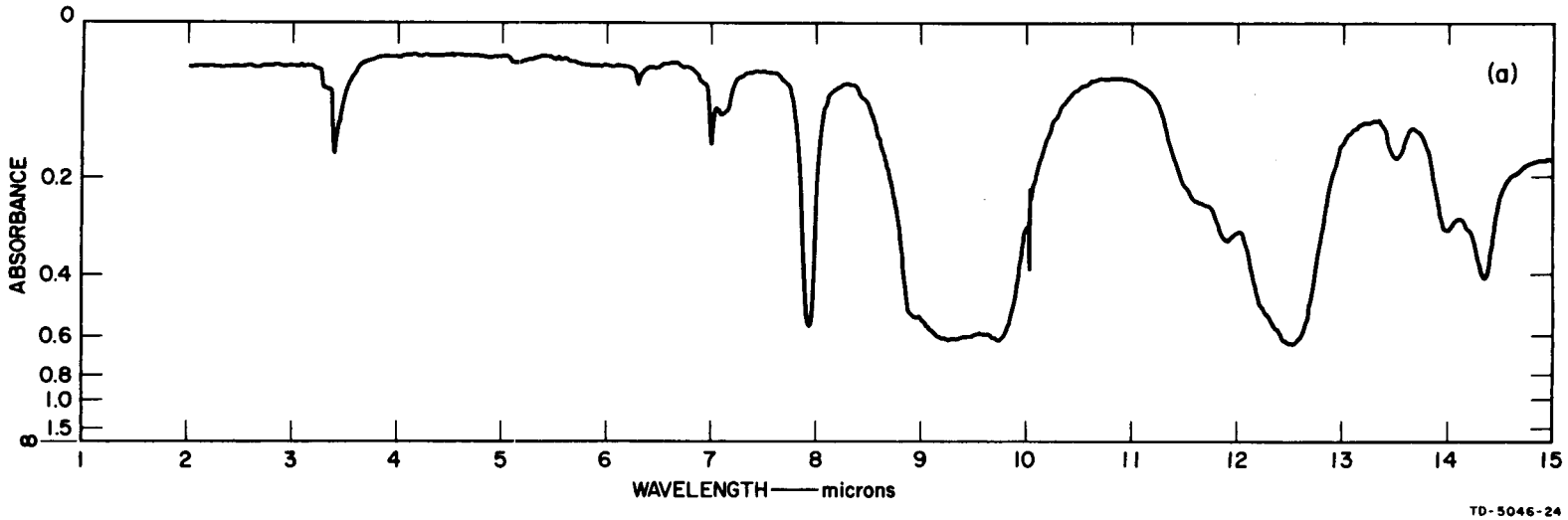

FIG. 21(a) INFRARED SPECTRUM OF RTV 511 FILM AFTER REMOVAL OF FILLER

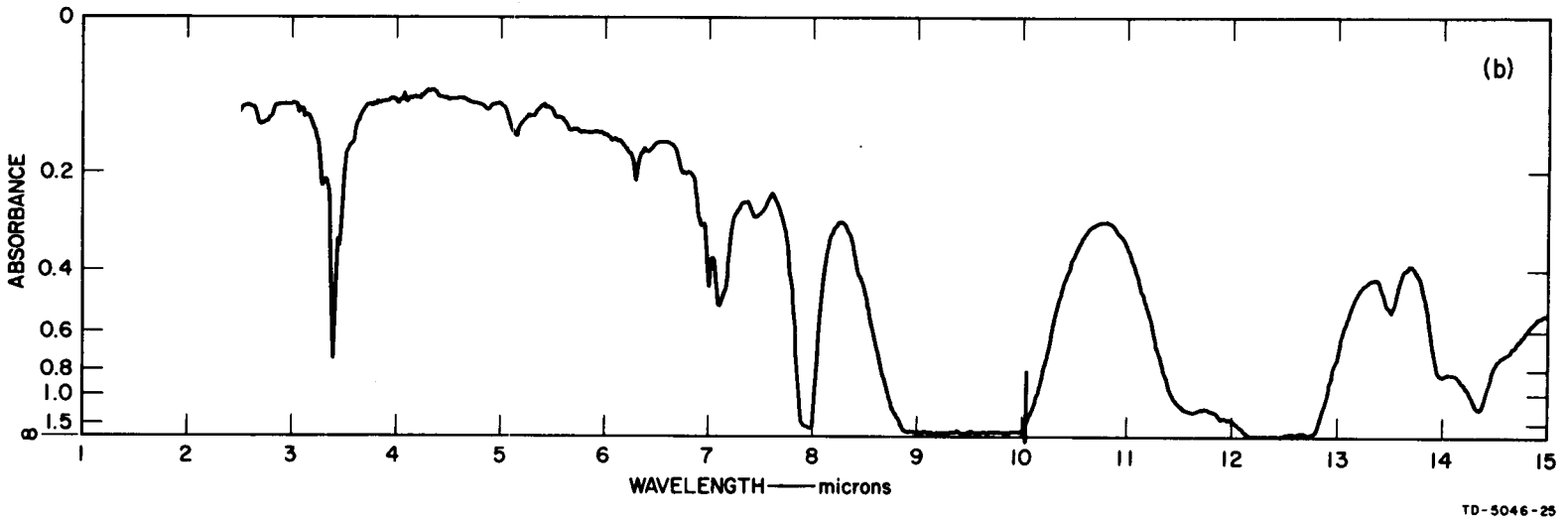

FIG. 21(b) INFRARED SPECTRUM OF OIL EVOLVED FROM AN RTV 511 TEST SAMPLE AT 150 °C AND 10^{-6} torr

D. POLYFLUOROCARBON FILMS

Many studies have been made of the behavior of Teflon (polytetrafluorethlene) in simulated space environments. Jolley and Reed[1] have reviewed over one hundred references on this subject, and numerous survey reports on the properties of TFE plastics have been published. Madorsky, et al.[2] have examined the thermal degradation of this material and several other fluorinated polymers in considerable detail. However, little information is available on the behavior of hydrofluorinated materials such as Tedlar [poly(vinyl fluoride)] in a space environment. Teflon TFE has been found to be stable up to 450°C under vacuum. Teflon FEP, which is also totally fluorinated, and differs only by the presence of CF_3 side chain on the polymer backbone, would be expected to be similar to Teflon TFE. The substitution of one or more hydrogen atoms for fluorine, however, alters the polymer considerably. For example, polyvinyl fluoride's weight loss at 240°C is similar to that of Teflon at 380°C.

Samples of Tedlar (polyvinyl fluoride) and Teflon FEP (copolymers of tetrafluoroethylene and hexafluoropropylene) film were obtained from E. I. du Pont de Nemours. Some properties of the various films are summarized in Table XXIII. The films were used as received from the manufacturer; sample weights and areas are given in Table XXIV.

Test Samples

Samples of Tedlar were cut into rectangles 3 x 10 cm; this sample size could be accommodated by the resin flasks without folding or curling. Because of the scatter of points observed in the testing of the Tedlar samples, the Teflon FEP samples were cut somewhat larger (6 x 22 cm and 3 x 22 cm) in an attempt to improve the accuracy of the weight loss determinations. These samples were rolled before placing in the resin flasks. Dust or foreign matter on film surfaces was removed by wiping with paper.

1. Space/Aeronautics, February 1963, p. 105.
2. J. Res. Nat'l Bur. Std., 51, 327 (1953).

TABLE XXIII

DU PONT TEDLAR AND TEFLON FEP FILMS USED IN WEIGHT-LOSS STUDIES

Material	Film Code	Film Type	Surface Characteristics	Thickness
Tedlar[a]				
TD 40/S	200 SG 40 TR, (trans.)	low shrinkage	both sides heat sealable	2 mil
TD 30/A	200 AG 30 WH, (white)	med tensile strength	one side adherable	2 mil
TD 30/B	200 BG 30 WH, (white)	med tensile strength	both sides adherable	2 mil
TD 20/A	50 AG 20 TR, (trans.)	high tensile strength	one side adherable	0.5 mil
Teflon FEP[b]				
FEP-a	500 A FEP			5 mil
FEP-b	500 A FEP			5 mil

[a] polyvinyl fluoride films

[b] copolymers of tetrafluorethylene and hexafluoropropylene

TABLE XXIV

WEIGHT AND DIMENSIONS OF POLYFLUOROCARBONS USED IN WEIGHT-LOSS STUDIES

Material	Sample No.	Area cm^2	eight, g
Tedlar	TD 40/S	60.0	0.26467
	TD 30/A	59.4	0.23683
	TD 30/B	60.0	0.25386
	TD 20/A	55.6	0.04744
Teflon FEP	FEP-a	260	3.37703
	FEP-b	130	1.67497

Effect of Exposure at 150°C and 10^{-6} torr on Polyfluorocarbon Films

Figure 22 shows the weight-loss curves of the polyfluorocarbon materials at 150°C and 10^{-6} torr. The scattering of points is due primarily to the small sample sizes and correspondingly small weight losses. It is believed that large fractions of the changes in weights of the samples are due to desorption of surface moisture and gases and subsequent resorption when reweighed in air. Continuous weighing under vacuum would, of course, be a superior method for this type of sample.

The most striking feature of the weight loss curves is the difference between the filled (pigmented) materials, TD 30/A and TD 30/B, and the unfilled transparent films. (See Table XXV.) Not only do the filled materials exhibit larger weight losses but in contrast to the others, they exhibit positive weight-loss rates. In view of the large scatter of data, the curves for TD 30/A and TD 30/B may be considered identical. These two materials differ from each other only in surface preparation, which apparently exerts no effect on the outgassing properties.

The samples of Tedlar [poly(vinyl fluoride)] behaved similarly to those of FEP. It was found, however, that the pigmented samples (30/A and 30/B) exhibited much higher weight losses than the transparent Tedlar films. These pigmented Tedlar films also exhibited finite rates of weight loss; this may indicate that the pigment employed is somewhat volatile or contains volatile contaminants. All the Tedlar films tested exhibited some discoloration. This darkening in color has been observed in conjunction with the degradation of poly(vinyl fluoride) and is believed to be due to the formation of conjugated unsaturation in the polymer as a result of the elimination of HF. The slight discoloration observed is, however, of little consequence. As in the case of poly(vinyl chloride), extremely large color changes may take place in the material without any structural changes being observable in the infrared spectra; i. e., degraded material constitutes less than about 1% of total sample.

The Tedlar test specimens all incurred a color change during thermal vacuum treatment, going from white or water-white to a light brown. The UV-visible spectrum from 2500 to 6500Å of TD 40/S before and after thermal vacuum treatment was examined; the spectral characteristics of the UV curve remained similar except for an overall increase in absorbance of the treated film. The much greater increase in the UV region suggests formation of conjugated systems $(-CH=CH-)_n$.

Because of the scatter of data, the method of least squares was applied on the assumption that a steady state was achieved in less than 24 hours. Table XXV summarizes the weight loss data; weight losses range from 0-0.5% by weight; weight loss rates are taken as zero for all materials except the pigmented Tedlars, 30/A and 30/B, which lose weight at a rate of approximately 0.001% per hour.

In view of the chemistry of these materials, it is obvious that polymer degradation would not be expected to be a significant factor, especially in the case of Teflon FEP. This is consistent with various observations that the weight-loss of this material at 150°C is indeed very low and is due primarily to desorption of surface contaminants such as water and carbon dioxide.

TABLE XXV

WEIGHT LOSS DATA FOR TEDLAR AND TEFLON FEP FILMS AT 150°C and 10^{-6} torr

Material	Sample	Initial Wt. Loss, %	Wt. Loss Rate % 100 hrs	% Wt. Loss after 200 hrs	rms Deviation %
Tedlar	TD 40/S	0.14	0	0.14	0.02
	TD 30/A	0.39	0.075	0.54	0.04
	TD 30/B	0.35	0.08	0.50	0.03
	TD 20/A	0-.05	---	0-.05	---
Teflon FEP	a	0.084	0	0.075	0.013
	b	0.003	0.02	0.05	0.008

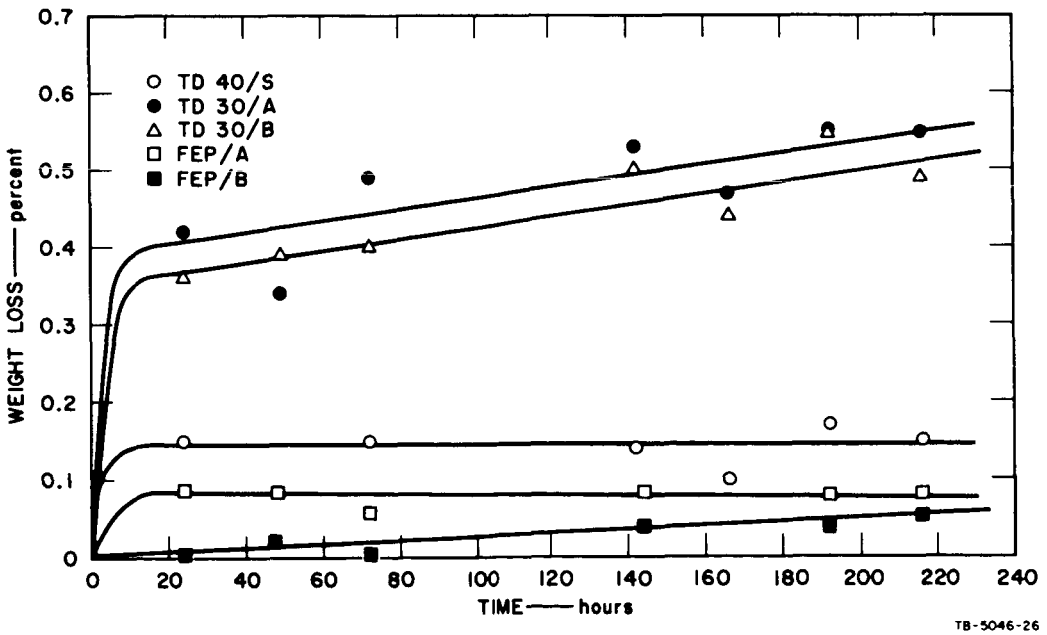

FIG. 22 PERCENT WEIGHT LOSS OF TEDLAR AND TEFLON FEP FILMS AT 150 °C AND 10^{-6} torr

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V. FUTURE WORK

The continuation of this program will permit the establishment of finalized operation and handling procedures for the vacuum weight loss test specifications as well as recommended handling procedures according to physical state in the materials specifications for various classes of polymers. Additionally, weight loss determinations will be performed for polymers of particular interest via vacuum thermogravimetric procedures; this will serve to verify the validity of the more simple means of determining loss of weight criteria. It is anticipated that weight loss limits will be established for a great number of polymeric materials.

As stated earlier, loss of weight of polymeric materials may affect their physical, mechanical, or electrical properties. Although some loss of weight can be attributed to release of absorbed gases which will be swept away into the vacuum of space, other released substances may deposit on adjacent, cooler surfaces of spacecrafts and thus affect the performance of electrical contacts, lenses and mirrors, etc. The quantity of such volatile condensable material (VCM) is then another important criterion in the selection of materials for spacecrafts. Prior work (Ref. 11, Part II) has shown the tenacity of VCM and suggested its adverse affects on spacecraft functions. Therefore, plans are underway to develop a simplified VCM apparatus which can be used for test specifications.

Many analytical methods are available for the determination of various chemical compositions and physical properties of organic materials; however, application to polymeric materials in general and specific polymer classes in particular may require very simple or quite drastic modifications in order to permit recommendations for test procedures which will be meaningful and reproducible. It is anticipated that as various classes of polymers are submitted for qualification, a file of reliable analytical procedures for polymeric materials will be developed.

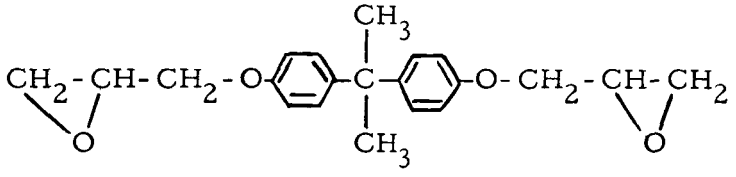
Suggestions for development of other test procedures will be made as the need becomes apparent or at the request of the JPL Cognizant Engineer.

Assistance will continue to be rendered in providing necessary background information or technical and editorial review toward the preparation of materials specifications and standardized test procedures.

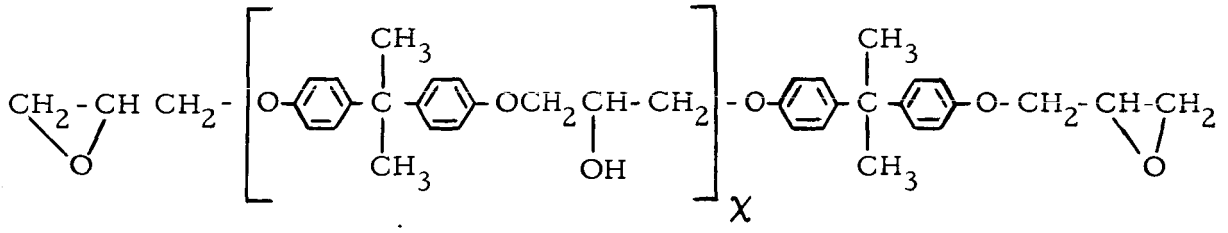
APPENDIX A

CHEMISTRY OF EPOXY RESINS

The Shell Company Epon adhesives are proprietary materials intended for engineering uses; thus, the chemical compositions of these adhesives are not well known. In general, they consist of three components; an epoxy base, a "hardener" or curing agent, and a filler. Of these, only the first two are chemically active. Using infrared spectroscopy, the epoxy base of several of the adhesives tested has been found to be identical to Epon 828, which is based on the diglycidyl ether of Bisphenol A; its structure is



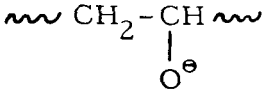
The commercial resin consists of low average molecular weight condensation products of the general structure:



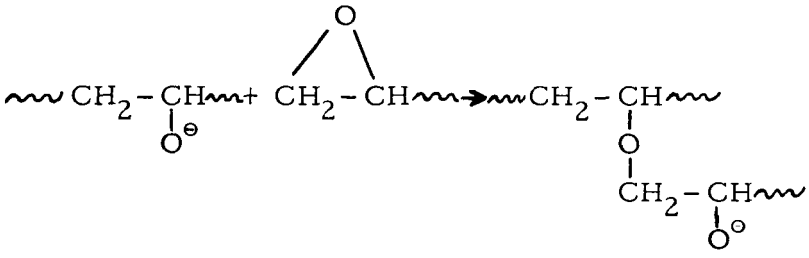
The linear polymer is cured, i. e., converted to the crosslinked resin, by use of a "hardener" or curing agent, which may be any compound having a basic group or reactive hydrogen.

Ethylenediamine and the higher polyethylene polyamines are often used as curing agents, as well as aliphatic amine salts of fatty acids which are indefinitely stable in the presence of the epoxy at room temperature but cure rapidly when warmed. Other common curing agents are acid anhydrides, such as succinic, maleic, phthalic, and pyromellitic.

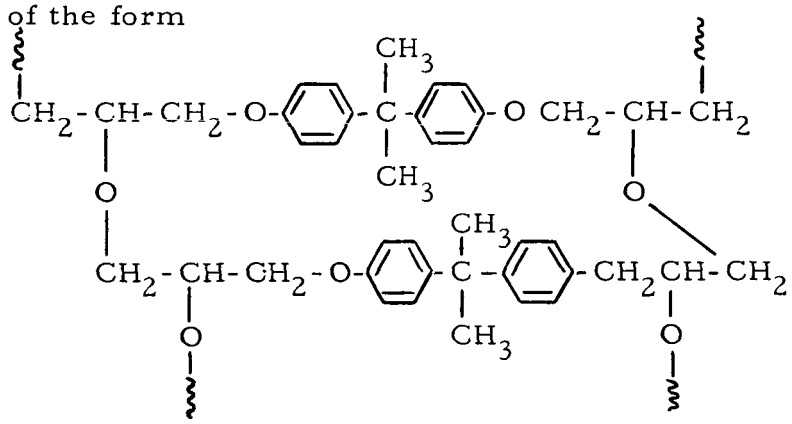
The mechanisms involved in the curing of epoxy resins are somewhat complex but fall into two general categories. The first gives the formation of a homopolymer where the curing agent (a base, often a tertiary amine) functions solely as a catalyst for the opening of the epoxide ring to give the species



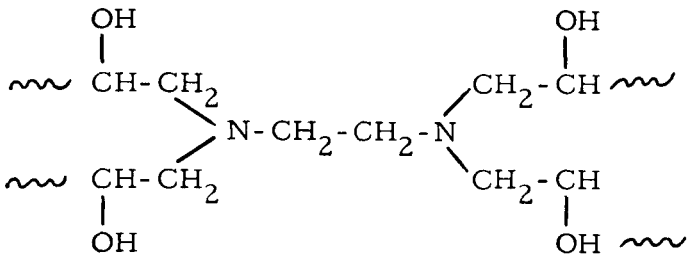
which, in turn, is capable of opening another epoxide ring



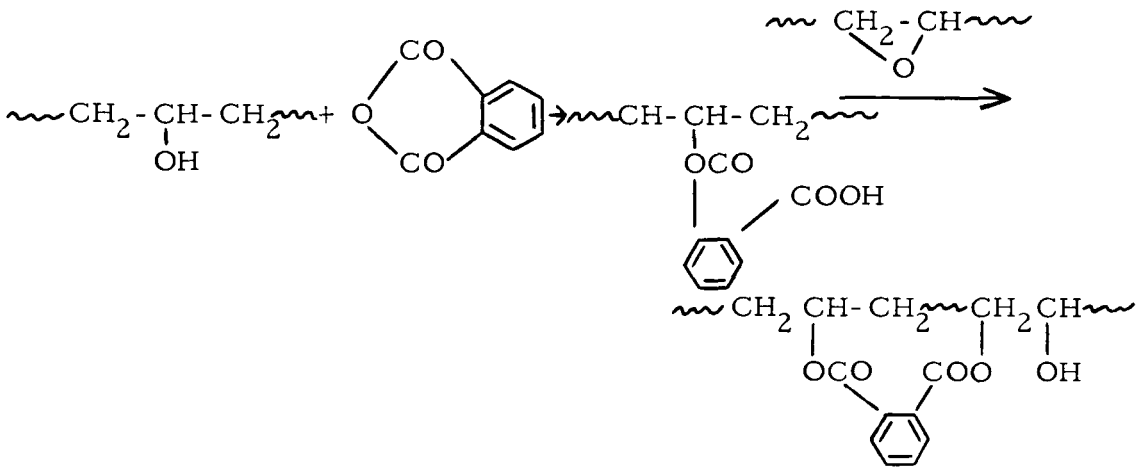
The reaction may then proceed to form an infinite, three-dimensional network of the form



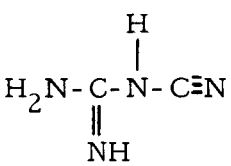
The second type of crosslinking reaction involves the incorporation of the curing agent into the epoxy network. The principal reactive crosslinking agents are dibasic acids or their anhydrides, or polyfunctional primary or secondary amines or amides. The simplest examples of this type of curing reaction is that with ethylenediamine. Each active hydrogen may react with an epoxy group, so that the final structure has the form



Dibasic acids react similarly to the amines, but the dibasic acid anhydrides have no active hydrogen and must attack first through a hydroxyl group. An example is the reaction with phthalic anhydride:



Dicyandiamide is a particularly important curing agent (employed in Epons 4224 and 914) of the structure



Its action is purely catalytic, i. e., it is not incorporated into the epoxy network. The mechanism of reaction is not well understood, but it is believed that catalysis is due to heat decomposition products of the dicyandiamide.

The discussion above is intended only as a general description of the types of epoxy curing reactions. In the case of the commercial resins used in this work, the structure of the curing agent is not generally known. Epons 901B-3 and 931 utilize an aromatic amine, 914 and 934 are cured with polyamides, 917 is anhydride-cured, and Epon 422J is a mixed epoxy phenolic resin; no information on the curing of Epon 903 is available.

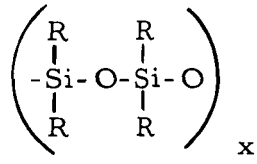
In addition, it must be pointed out that the Bisphenol A-based epoxy (Epon 828) is not the only resin base used. Epons 934 and 931 are novel epoxide system based on diols other than Bisphenol A.

Fillers are classed as metallic or non-metallic; the former is generally aluminum, the latter may be alumina or silica or asbestos powder.

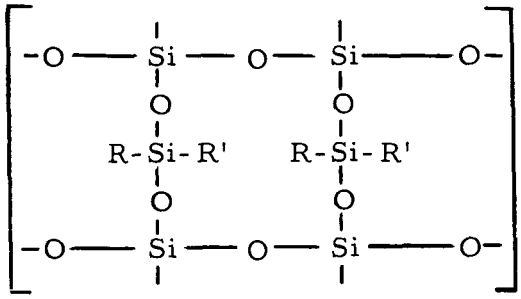
APPENDIX B

CHEMISTRY OF (POLY)SILOXANES

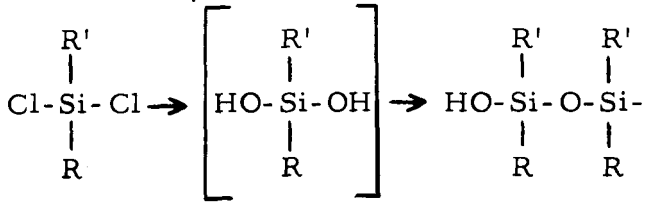
The silicone polymers discussed in this report are based on the polymeric siloxane structure



Where R is either phenyl or methyl. The linear polysiloxanes range from fluids to gums depending on their molecular weight, and may be crosslinked under certain conditions to form a polymer network of the form



The intermediate in the formation of the siloxanes is the hydroxysilane, formed by hydrolysis of the corresponding chlorosilane.



The materials discussed in this report all have methyl as the R group; R' may be either another methyl, as is the case for RTV 60 or 11, or it may be phenyl, as for RTV 511 or 560. The phenyl and methyl silicones have a number of properties which render them especially suitable for commercial applications; of particular interest for space application

is their high heat stability, accompanied by retention of physical properties, such as flexibility, over a broad temperature range (-70° to 250°C). They are also chemically inert and very stable toward oxidation.

The silicone rubbers are crosslinked structures. The silicone preparation obtained from the manufacturer consists of a mixture of a long chain siloxane gum, an inorganic filler, and an oxidizing agent or catalyst. Dibutyl tin dilaurate was employed in all polymers studied.

In the room-temperature-cured materials, crosslinking takes place between the hydroxy silane chain ends and alkoxyl groups on a crosslinking agent:

$$\equiv Si\text{-}OH + RO\text{-}Si\text{-}OR + HO\text{-}Si\equiv \xrightarrow{\text{Catalyst}} \underset{\displaystyle \equiv Si\text{-}O\text{-}\underset{\displaystyle |}{Si}\text{-}O\text{-}Si\equiv}{} + 2\ ROH \qquad (I)$$

A second type of room-temperature-cured rubber is kept in a closed container, such as a tube, until used. On exposure to atmospheric moisture, the rubber cures as a result of hydrolysis of the acetyloxy group:

$$\equiv Si\text{-}O\text{-}COR + HOH \longrightarrow \equiv Si\text{-}OH + RCOOH \qquad (II)$$

The hydroxyl group is then available for crosslinking. The one-part adhesive sealants, RTV 102, 106, 108, and 112 are undoubtedly of this type.

Under high vacuum, the pure siloxane polymer is stable to 350-400°C; at higher temperatures the Si-O bonds are broken and reform as volatile, low molecular weight fragments. In commercial silicones the degradation temperature is much lower, primarily because of the presence of impurities in the polymer. In practice it has been found that thermal stability is also sensitive to moisture, oxygen, and oxidants, as well as trace impurities.